



OPTIMIZATION OF PT-DOPED KOCITER ELECTRODES

IN H₃PO₄ FUEL CELLS

by

L. B. Welsh, R. W. Leyerle

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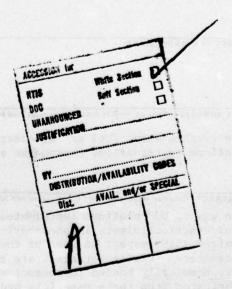
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Kocite materials were produced in 200-400 gram quantities from high-surface-area aluminas with a particle size of 500 nm. From the platinum-impregnated Kocite electrocatalyst, Teflon-bonded electrodes with porous, graphite-paper backing were fabricated by machine-calendering techniques. These electrodes had platinum loadings ranging from 0.22 to 0.58 mg/cm. When tested in model phosphoric acid fuel cells with 2 mg/cm² platinum black counter electrodes, full-cell IR-free performances of 0.70 and 0.77 volts as air and oxygen cathodes, respectively, have been obtained at 100 ma/cm² and 180°C using a 0.54 mg/cm² platinum electrode as a cathode in a cell with a silicon carbide matrix. Full cell IR-free performance of 0.67 and 0.74 as air and oxygen cathodes, respectively, have been obtained at 100 ma/cm² and 180°C using a 0.42 mg/cm² platinum loaded electrode as the cathode in a cell with a Kynol matrix. Lifetime testing of Kocite electrodes as cathodes indicates no catalyst deterioration occurs for periods in excess of 500 hours for temperatures from 150 to 180°C.

Under fuel cell operating conditions the electrolyte leaches the alumina substrate from the electrocatalysts, but no instability in cell performance appears to result. Measurements of the platinum particle sintering rate indicate a lower sintering rate for platinum on leached Kocite electrocatalysts than on platinum-doped carbon-black electrocatalysts having similar Pt/C ratios. Anodes incorporating Kocite electrocatalysts have shown better short term tolerance to a 5% CO contamination in the H₂ gas than 2 mg/cm platinum black anodes when operated comparably.

To optimize the structure of Kocite electrodes, the platinum loading, Teflon content, and the catalyst layer density and thickness have been systematically varied. Test results indicate that the cell performance is directly proportional to the platinum loading. The optimal value for the Teflon loading is a weight ratio of ~1:1 to the leached electrocatalyst. The performance does not change substantially with variations of the catalyst layer density or thickness.



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I. INTRODUCTION

1.1 Objectives

The objective of this program was to optimize the performance of low-cost air and fuel electrodes fabricated from platinum-impregnated proprietary UOP Kocite materials for use in phosphoric acid electrolyte fuel cells within the temperature range of 140-180°C. To accomplish this objective, various Kocite formulations were produced and fabricated into state-of-the-art fuel cell electrodes. These electrodes were tested as anodes or cathodes in model fuel cells with conventional platinum black electrodes as counter electrodes. Long term (500 hour) endurance testing was completed on promising electrodes.

This report summarizes the results obtained during this 15 month program. The fuel cell performance levels achieved during this period using fuel cell electrodes fabricated from platinum-doped Kocite materials will be discussed, along with recommendations for future research.

1.2 Background

The current research program followed an evaluation of the performance of Kocite^R materials in fuel cell electrodes for phosphoric acid electrolyte fuel cells^(1,2) completed under USA/MERADCOM contract number DAAKO2-75-C-0011. The program organization established under this previous contract was continued. This involved a joint program with

L. B. Welsh, G. L. Hervert, D. H. Spielberg, K. J. Youtsey, "Carbonaceous Catalysts for H₃PO₄ Fuel Cells", MERDC Contract DAAKO2-75-C-0011, Interim Technical Report, March, 1975.

²L. B. Welsh, R. W. Leyerle, G. L. Hervert, and K. J. Youtsey, "Carbonaceous Catalysts for H₃PO₄ Fuel Cells", MERDC Contract DAAKO2-72-C-0011, Final Technical Report, September, 1975.

UOP Inc. as the prime contractor and Energy Research Corporation (ERC, a subsidiary of St. Joe Minerals Corporation) as subcontractor. A broad division of effort was made on the basis of the UOP capability to produce Pt-impregnated Kocite materials and the ERC capability to fabricate and optimize electrode structures. Testing and diagnostic evaluation of these electrodes were carried out jointly by UOP and ERC.

1.3 Review of Previous Results

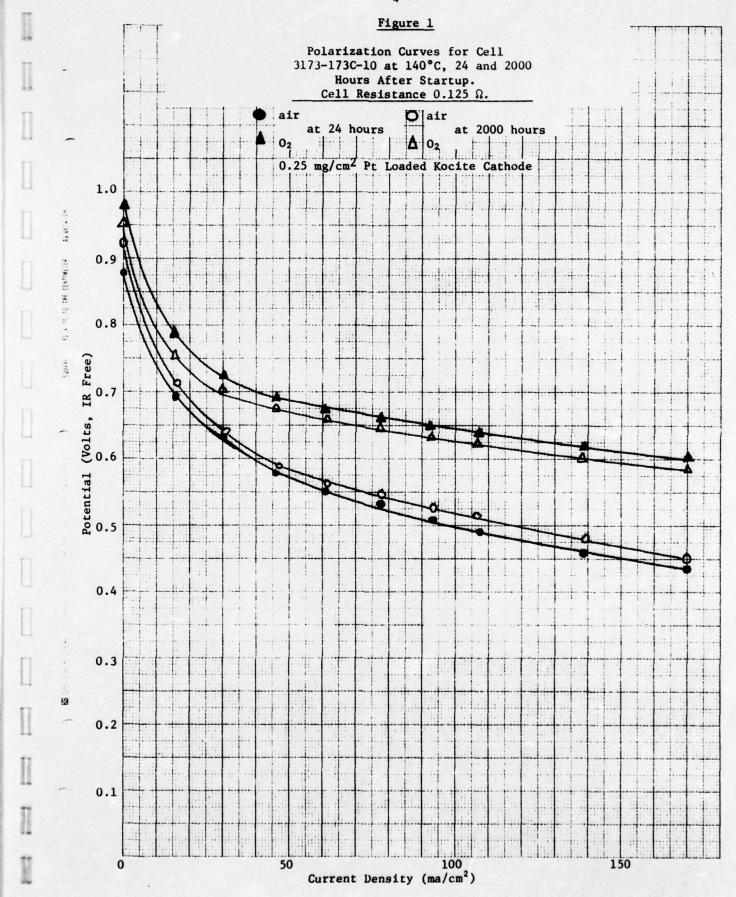
1.3.1 Kocite^R Materials

Kocite Materials are composite structures consisting of a thin film, semiconducting pyropolymer chemically bonded to the surface of an electrically insulating, high surface area, refractory substrate. The materials used to produce Kocite powders can vary widely but commonly include gamma alumina as the refractory substrate and hydrocarbons such as cyclohexane and benzene as the pyrolyzable material or pyropolymer precursor. Pyrolysis temperatures are commonly in the range of 400 to 900°C. The electrical conductivity of Kocite materials can be varied widely in a controlled manner by adjusting one or more of the following parameters: (a) substrate composition and surface area, (b) pyrolyzable material, and (c) reaction conditions (e.g., reaction time, temperature, ambient gases). The electrochemical behavior may also depend on these parameters. The current application of Kocite materials to fuel cell electrocatalysts consists of their utilization as high surface area extenders and supports for catalytically active materials (transition metals, etc.). The preparation of Kocite materials and their analysis have been discussed in earlier reports. (1,2)

1.3.2 Program Status at the Inception of the Present Contract

The intent of the previous contract (DAAKO2-75-C-0011) was to evaluate Kocite materials as electrocatalysts for use in H₃PO₄ fuel cell electrodes. (1,2) However, Kocite materials were found to have little electrocatalytic activity. Kocite materials were then evaluated as catalyst metal supports. During the remaining period of the previous contract, fuel cell electrocatalysts were produced from small particle size Kocite materials by impregnating them with platinum. These electrocatalysts were then fabricated into electrodes and evaluated in model fuel cells. This evaluation indicated that Kocite materials could be used as stable extenders or supports for catalytically-active metals in H₃PO₄ fuel cell electrodes at 140°C.

The best performance of a Kocite-containing electrode (2) achieved prior to the inception of the present contract is shown in Figure 1. In this figure, IR corrected full cell polarization curves are shown. The data were obtained using a Kocite cathode with 0.25 mg/cm² Pt loading and a 2 mg/cm² platinum black electrode as the anode. Comparison of the curves at 24 and 2000 hours shows the full cell stability achieved at that time. Though the performance of the cell at 100 ma/cm² on oxygen dropped after 2000 hours, the air performance increased by 25 mV. The cause of this performance change was unclear, but was not a result of any obvious deterioration of the electrode or cell components. The cell voltage of 518 mV was the highest performance obtained at 100 ma/cm² and 140°C during the previous contract.



Before the start of the present contract, sufficient lifetime testing (500 hours) at 140°C had been done to indicate that Kocite electrodes performed without deterioration as air or oxygen cathodes. However, the oxygen gain of the cells at 100 ma/cm² was larger than desired, indicating gas diffusion losses in the electrode. From cell performance results obtained with electrocatalysts made with Kocite materials having different particle sizes, it was clear that use of smaller alumina particles and optimization of electrode structure would reduce these gas diffusion losses. Preliminary cell testing was also performed at 180°C, where air cathode performance improved substantially. Limited lifetime testing indicated that Kocite cathodes perform stably at temperatures as high as 180°C. As hydrogen anodes, the initial performance of Kocite electrodes was encouraging, but the performance decayed quickly, possibly as a result of poisoning.

1.3.3 Results Obtained During the First Five Month Period

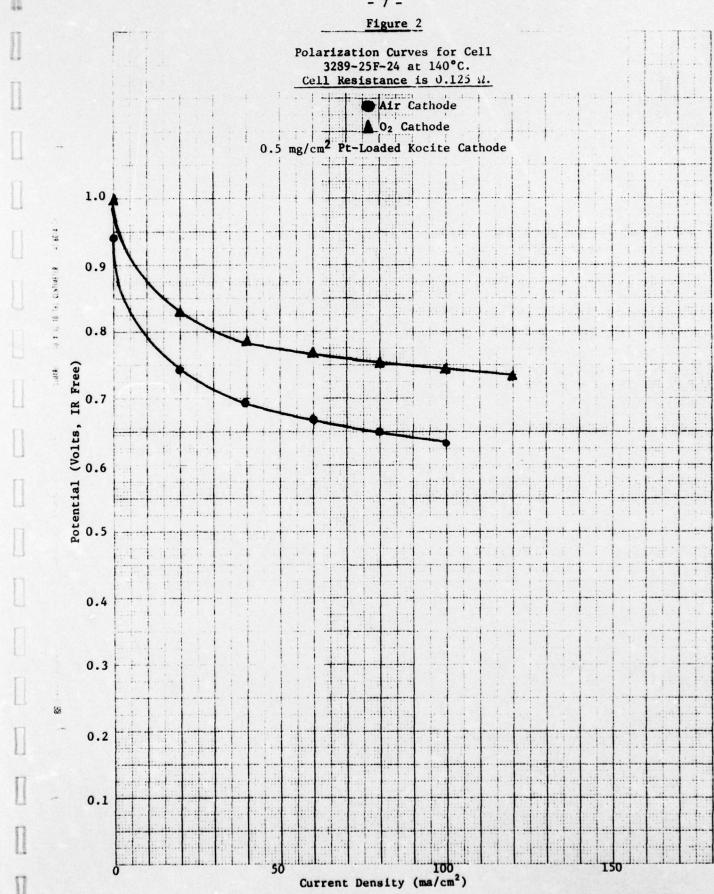
The major effort during the first five months of this contract was devoted to electrocatalyst development. $^{(3)}$ In particular, comparisons were made between electrocatalysts prepared using two different alumina substrates. Several batches of Kaiser Medium Alumina were ground and size classified to obtain base material having mean particle sizes of $1-2.5 \times 10^3$ nm. This is the same base that was used at the end of the previous contract for the 3173-173 series

³ L. B. Welsh, R. W. Leyerle, G. L. Hervert, "Optimization of Pt-Doped Kocite Electrodes in H₃PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, March, 1976.

electrocatalyst batches. The other base material, Alcoa's Hydral 705, was tested because it had a smaller mean particle size (\sim 500 nm), a different pore volume distribution⁽³⁾, and was commercially available. Both the particle size and the pore size of the resulting Kocite materials can substantially effect the performance of the electrocatalyst, particularly due to losses resulting from diffusion limitations.

Improvements made in production techniques and electrocatalyst structure resulted in increased performance levels of Kocite electrodes. The best performance level achieved during this period was obtained with a cell containing a cathode fabricated from electrocatalyst batch 3289-25F. This electrode had a platinum loading of 0.5 mg/cm², twice the loading of any previously tested electrode. The cell operated at an IR corrected voltage of 0.63 on air and 0.74 on oxygen at a current density of 100 ma/cm² at 140°C. Results obtained with this cell, shown in Figure 2, are 100 mV better than the best results obtained prior to this contract period, shown in Figure 1. However, the 110 mV O₂ gain of this cell was still larger than desirable.

The first Kocite material produced from the smaller Hydral alumina base material was batch 3380-31. A cell containing a 0.25 mg/cm² Pt-loaded cathode fabricated from catalyst batch 3380-31B operated at the highest performance level measured at that time for that Pt-loading. Full cell polarization curves for this cell are



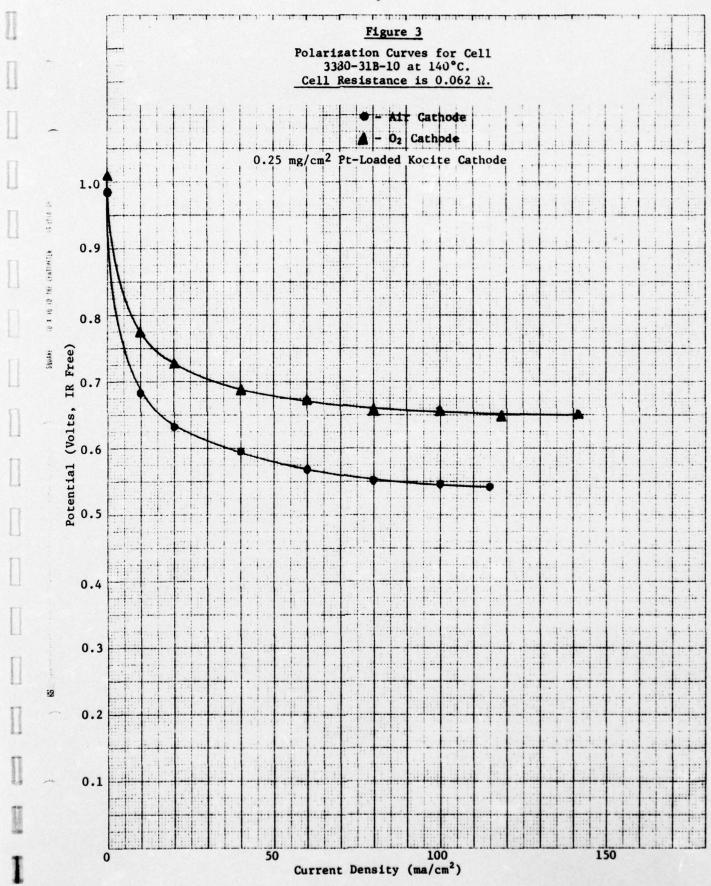
shown in Figure 3. At 140°C and 100 ma/cm², IR corrected voltages of 0.55 V on air and 0.66 V on oxygen were obtained. This air cathode performance level is about 30 mV better than the best electrode performance at the inception of this contract for the same cell temperature and platinum loading.

Cells with Kocite air cathodes were proved stable at current densities of 100 ma/cm² for periods in excess of 500 hours at temperatures ranging up to 180°C. One cell, containing an electrode from electrocatalyst batch 3289-25F, maintained an IR corrected voltage of 0.585 V for 500 hours at 160°C. The terminal voltage of this cell rose from 0.515 to 0.520 V during that time. Another cell, operating at 180°C with a similar electrode used as an air cathode, had a 25 mV decrease in its terminal voltage over 500 hours, but its IR corrected voltage was steady at 0.640 V.

Facilities were completed during this five month period for the production of Kocite materials in batches of 300 g or more. These large batches allowed ERC to prepare electrodes using machine calendering techniques which improve electrode uniformity and reproducibility.

1.3.4 Results Obtained During the Second Five Month Period

The main effort during this period was to optimize the performance of Kocite electrodes produced from a single electrocatalyst batch. Systematic variations of certain electrode structure

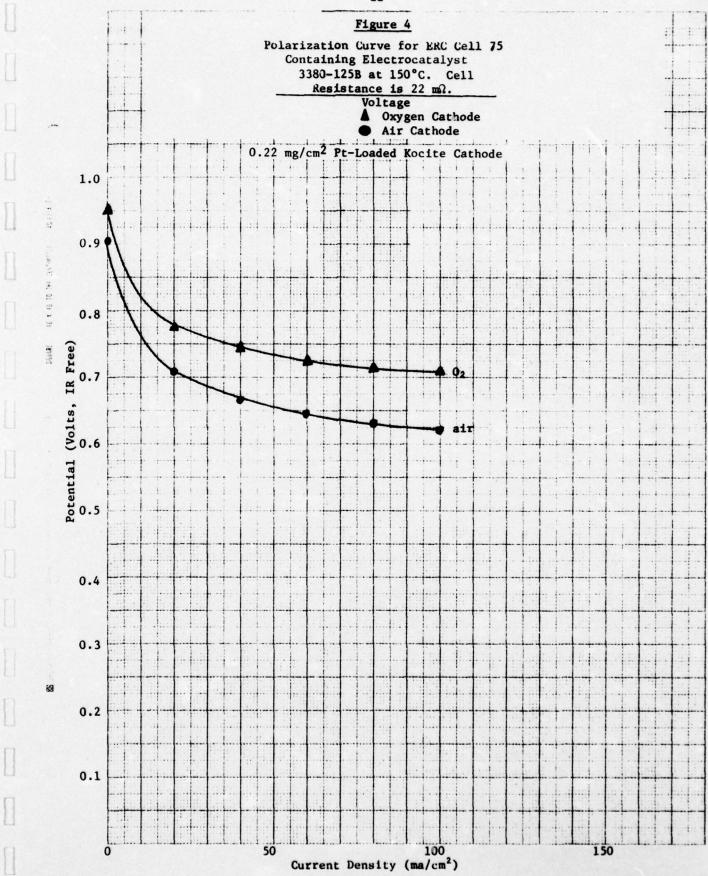


parameters such as teflon loading, catalyst loading, and catalyst layer density were made to determine the optimum electrode production parameters for machine calendered electrodes. (4) Electrocatalyst batch 3380-125B was used for these electrodes. The improvement achieved in cell performance during this period is illustrated in Figure 4, for a cell with a 0.22 mg/cm² Pt-loaded cathode containing electrocatalyst batch 3380-125B. At a current density of 100 ma/cm², the IR corrected cell voltage was 0.62 V on air and 0.71 V on oxygen at 149°C. The O₂ gain decreased to 90 mV. At 149°C, the performance of this cell on air at 100 ma/cm² was 100 mV higher than that of the cell operating at 140°C shown in Figure 1. This performance was also 80 mV higher than the best cell of the first five month period, shown in Figure 3 (0.25 mg/cm² Pt loading).

For the first time, during this period a stable performance was achieved by a cell having a Kocite anode. A cell, with an anode containing electrocatalyst batch 3289-25F, showed no deterioration of its IR free voltage after 500 hours of operation at 100 ma/cm² at 180°C. This cell had a 2 mg/cm² platinum black electrode as its air cathode.

The performance of Kocite electrodes having different electrode structures was studied during this period to determine the

⁴L. B. Welsh, R. W. Leyerle, "Optimization of Pt-Doped Kocite^R Electrodes in H₃PO₄ Fuel Cells", MERADCOM Contract DAAG53-76-C-0014, Interim Technical Report, August, 1976.



optimum electrode structure. The teflon content of the electrodes was varied from 20 to 50 wt.% (based on the Kocite loading) and the performance of a large number of these electrodes was measured. In general, better performance was obtained (4) from cells containing electrodes having teflon contents below 40 wt.%. In addition, the cells achieved peak performance much more rapidly when electrodes were used having the lower teflon loading. Medium density electrodes gave better performance than low density electrodes (4), for which the catalyst layer often did not properly adhere to the carbon-paper backing. Variation of the catalyst layer thickness indicated that the use of thinner catalyst layers might improve electrode performance. Results obtained during the third five month period confirmed that lower teflon-loaded, medium density electrodes had superior performance characteristics, but the use of thinner catalyst layers did not improve electrode performance.

1.4 Program for the Last Five Month Period

The primary effort during this period was the continued testing of electrodes with differing electrode structure, fabricated from the same electrocatalyst batch. Experimentation was completed with catalyst batch 3380-125B and extensive testing was done with catalyst batch 3380-156G using electrodes loaded with $\sim 0.5 \text{ mg/cm}^2$ platinum. These electrodes have shown significantly higher performance and better stability than previous electrodes. Work was performed during the last five month period in the following areas.

- (A) Using large batches of Kocite electrocatalysts, numerous electrodes have been fabricated by machine calendering to assess the effects of electrode structure variation and determine the optimum electrode structure. Cathode performance data have been taken at 150, 160, and 180°C. The parameters which have been varied include,
 - 1) platinum loading
 - 2) teflon content
 - 3) catalyst layer thickness
 - 4) catalyst layer density (bonding pressure)
- (B) Tests were conducted to determine the extent of substrate leaching by phosphoric acid.
- (C) Limited anode testing has been performed at 160 and 180°C. The short term tolerance of Kocite anodes to a 5% CO contamination in the hydrogen fuel gas has been determined and compared with the CO tolerance of platinum black electrodes. A cell consisting of Kocite electrodes as both the cathode and anode was also tested successfully.
- (D) Substantial air cathode lifetime test data have been accumulated. As an example, stable performance has been obtained for cells with Kocite cathodes operated for over 4000 hours at 150°C and for over 2500 hours at 180°C.
- (E) The rates of platinum particle sintering on Kocite electrocatalyst powders and Kocite electrodes were determined by X-ray diffraction techniques.

A detailed discussion of the results obtained in each of these areas is presented in the following sections.

II. PT-DOPED KOCITER ELECTROCATALYSTS

The preparation and physical properties of the platinum-doped Kocite batches, from which electrodes have been fabricated, are discussed in this section. Some of these properties are listed in Table I. As the general preparation and platinum impregnation techniques have been discussed in earlier reports (1-4), only specific alterations of these techniques will be discussed here.

Three different alumina base materials were used to prepare the electrocatalysts listed in Table I. The 3173-173B, 3173-173C, and 3289-25F batches were prepared from Kaiser Medium Alumina ground to a mean particle size of $\sim 2.2 \times 10^3$ nm, while batch 3380-104B is made using the same alumina ground to a mean particle size of $\sim 1.2 \times 10^3$ nm. The other batches were made from Hydral 705 alumina with a mean particle size of 500 nm. As discussed in an earlier report (3), the pore volume distributions of these electrocatalysts are quite different. The Kaiser based materials have a broad, two peaked distribution with peaks near 4.0 and 8.0 nm, while the Hydral based materials have a narrow distribution with a single peak near 4.0 nm. From the results reported earlier (1-4), both the pore volume distribution and mean particle size are expected to affect electrode performance.

For the same surface area and resistivity, the carbon content of a Hydral-based Kocite material is substantially smaller than that of a Kaiser-based Kocite material. Typical carbon contents are about 35 wt.% for the Kaiser-based Kocite materials and 24 wt.% for the Hydral-based Kocite materials.

Table I
Characteristics of Pt-Impregnated Kocite Preparations

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Batch Number	3173-1738	3173-1730	3289-25A	3289-25F
Analysis, Wt. %				
Carbon Content of Kocite Material	34.7	33.20	36.80	36.80
Pt/(Pt + C)	5.50	13.1	8.96	22.9
Physical Characteristics				
р @ 25°C, Ω-сm	0.017	0.014	0.083	0.051
Apparent Bulk Density, g/ml	0.343	0.375	0.30	0.30
Surface Area, M/8	69	81	02	02
Pore Volume, m1/g	0.18	0.19	0.18	0.18
Average Pore Diameter, nm	10.4	9.6	10.3	10.3
Kocite ^R Substrate				
Type	γ -Al ₂ 0 ₃ (Kaiser)	γ -Al ₂ 0 ₃ (Kaiser)	Y-Al ₂ 0 ₃ (Kaiser)	γ -Al ₂ 0 ₃ (Kaiser)
Size Range, 10 ³ nm	2.2	2.2	1.2	1.2
Pyrolysis Temperature (°C)	006	006	006	006
Pyropolymer Precursor	CeHe	CeHe	CeHe	CeHe
Pt Addition	To Product	To Product	To Product	To Product
Pt Reduction Temperature (°C)	260	260	260	260

Table I (Cont'd)
Characteristics of Pt-Impregnated Kocite R Preparations

Batch Number	3380-31B	3380-31E	3380-31F	3380-31K	3380-65A
Analysis, Wt. %					
Carbon Content of Kocite Material	25.09	24.09	24.09	24.09	42.20
Pt/(Pt + C)	17.1	35.7	17.71	17.9	28.7
Physical Characteristics					
p @ 25°C, n-cm	0.0365	0.036	0.0365	0.036	900.0
Apparent Bulk Density, g/ml	0.28	0.28	0.28	0.28	0.85
Surface Area, M/g	69	69	69	69	59
Pore Volume, m1/8	60.0	0.09	0.09	0.09	0.15
Average Pore Diameter, nm	5.2	5.2	5.2	5.2	6.6
Kocite ^R Substrate					
Lype	$\gamma + \chi Al_20_3$ (Hydral)	$\gamma + \chi Al_2 0_3$ (Hydral)	$\gamma + \chi Al_2 0_3$ (Hydral)	$\gamma + \chi - Al_20_3$ (Hydral)	Y-Al ₂ 0 ₃ (Kaiser)
Size Range, 103 nm	0.5	0.5	0.5	0.5	2.2
Pyrolysis Temperature (°C)	850	850	850	850	006
Pyropolymer Precursor	CeHe	Сене	CeHe	CeHe	CeHe
Pt Addition	To Product	To Product	To Product	To Product	To Product
Pt Reduction Temperature (°C)	260	260	250	260	250

Table I (Cont'd)

Parameter &

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Characteristics of Pt-Impregnated Kocite Preparations

Batch Number	3380-104B	3380-104н	3380-125B	3380-156E	3380-156G	3380-180E
Analysis, Wt. %						
Carbon Content of Kocite Material	37.3	37.3	19.08	21.31	21.31	22.24
Pt/(Pt + C)	11.7	12.4	21.1	33.6	34.8	52.9
Physical Characteristics						
p @ 25°C, n-cm	0.032	0.032	0.13	0.11	0.11	0.13
Apparent Bulk Density, g/ml	0.398	0.398	0.30	0.29	0.29	0.25
Surface Area, M/8	62	79	80	81	81	78
Pore Volume, ml/g	0.17	0.17	0.11	0.11	0.11	0.11
Average Pore Diameter, nm	9.8	8.6	5.5	5.4	5.4	9.6
Kocite R Substrate						
Type	Y-Al ₂ 0 ₃ (Kaiser)	γ -Al ₂ 0 ₃ (Kaiser)	γ + χ -Al ₂ 0 ₃ (Hydral)	γ + χ -Al ₂ 0 ₃ (Hydral)	γ + χ -Al ₂ 0 ₃ (Hydral)	Y+X-A1 ₂ 0 ₃ (Hydra1)
Size Range, 103 nm	1.2	1.2	0.5	0.5	0.5	0.5
Pyrolysis Temperature (°C)	860	860	800	800	800	800
Pyropolymer Precursor	CeHe	CeHe	CeHe	CeHe	CeHe	CeHe
Pt Addition	To Product	To Product	To Product	To Product	To Product	To Product
Pt Reduction Temperature (°C)	260	260	260	260	260	260

The platinum impregnation of Kocite materials has been described in earlier reports. (1-4) In order to determine if each electrocatalyst has been prepared with a high platinum dispersion, an X-ray linewidth analysis of the platinum crystallite size was performed. The results of this analysis are given in Table II for the electrocatalysts listed in Table I. The percentage of Pt particles having diameters between 2.5 and 100 nm can be determined, as well as the average diameter of the Pt particles in this size range, when the X-ray data are compared against those of a standard. The numbers listed under agglomeration give the fraction of Pt atoms in Pt particles with a diameter greater than \sim 2.5 nm. The numbers are only relative because particles smaller than \sim 2.5 nm diameter are not measured as contributing to the Pt X-ray linewidth. The agglomeration numbers are normalized as discussed in an earlier report. (2) With a 5 wt.% Pt concentration, a typical agglomeration number is about 10% for both the Kaiser and Hydral based electrocatalysts with good Pt dispersion.

During the third five month period of the contract, evidence has been found that at fuel cell operating temperatures, phosphoric acid dissolves the alumina substrate of Kocite materials. For one material tested, only the carbonaceous pyropolymer layer remained after leaching and it had a surface area of $\sim 700~\text{m}^2/\text{g}$. The rate of leaching depends on the temperature, Kocite material particle size, and the thickness of the pyropolymer layer. All the alumina is leached from the electrocatalysts used during this contract period when they are used in operating fuel cells for 500 hours. This leaching does not appear to degrade the fuel cell performance since many cells increase their voltage over the first few hundred hours in the

Table II

Tongood P.

X-ray Analysis of Pt Crystallite Size

Kocite	Crystallize Size Nominal Diameter (nm)	Agglomeration	Pt/(Pt + C)
3173-173B	13.0	0.02	5.50
3173-1730	6.0	0.10	13.1
3289-25F	3.4	0.03	22.9
3380-31B	3.2	0.22	17.1
3380-104B	5.1	0.10	11.7
3380-104н	0.9	0.26	12.4
3380-125B	4.4	0.12	21.1
3380-156E	7.5	0.31	33.6
3380-1566	9.9	0.22	34.6
3380-180F	12.2	0.39	52.9

Mean size of crystallites over 2.5 nm diameter.

 $^{\mathrm{b}}$ These results are standardized as discussed in Reference 2.

same way that platinum impregnated carbon black electrode-containing cells do. This increase is probably due to increased wetting of the electrocatalyst layer, rather than the leaching. When the alumina is removed, the effective platinum loading of the resulting platinum impregnated carbonaceous pyropolymer electrocatalyst increases. For this reason all electrocatalyst platinum levels are listed on the basis of the Pt-Carbon content rather than the Pt-Carbon-Al₂O₃ basis used in the earlier reports. (1-4)

This change is noted in Table I and in the tables in Section 4.

The electrode platinum loadings remain the same.

III. ELECTRODE FABRICATION AND TESTING

3.1 Electrode Fabrication

The fabrication techniques used by ERC to prepare gas diffusion fuel cell electrodes containing Kocite electrocatalysts are similar to those used to prepare ERC platinum black electrodes. The process begins with the wet blending of the electrocatalyst with a dry PTFE powder and a filler within a petroleum distillate type of medium. Considerable care must be taken during this step to prevent any Kocite particle agglomeration. After filtration of the solids, a catalyst layer is formed by a calendering operation which can be accomplished either by hand rolling or with a machine rolling mill. To improve handling during the calendering process, a decomposable filler such as ammonium bicarbonate is used. After complete vaporization of the petroleum distillate, the filler is removed by gentle heating.

The remaining steps of electrode fabrication involve pressing, mounting on a current collector, and sintering. Some variation has occurred in these steps over the duration of this program. Initially the catalyst layer was pressed at 2000 psi (high density) onto a tantalum screen current collector. More recently, a highly porous and conductive carbon fiber paper such as produced by Union Carbide Corporation or Stackpole Carbon Company has been used as a less expensive alternative to the tantalum screen current collector. The carbon fiber paper is generally wetproofed to a certain degree prior to use, by treatment with FEP, a copolymer of tetrafluoroethylene and hexafluoropropylene. The pressure at which the catalyst layer is bonded to the current collector has also been varied. In the first five month period (3) low,

medium, and high density catalyst layers were prepared at 100, 500, and 2000 psi. During the later ten month period a different set of bonding pressures has been used for the machine calendered electrodes. During this period these electrodes have been prepared at 2000 psi (high density), 100 psi (medium density), and by using a different filler processing step (low density). Machine calendered electrodes have only been used with medium and low densities.

Following the electrode bonding step, the electrode is normally sintered in a nitrogen atmosphere at 345°C for 15 minutes. Electrodes prepared before the 3380-104B and 3380-125B electrocatalysts batches were sintered at 335°C.

The final thickness of the Kocite electrocatalyst layer depends on the bonding technique and pressure. For electrodes prepared during the last ten months, a 5 mg/cm² loading of Kocite powder and 50 wt.% PTFE content resulted in catalyst layer thicknesses of 0.004", 0.006", and 0.010" for the high, medium, and low density machine calendered catalyst layers, respectively. This thickness decreases as the PTFE content decreases.

3.2 Cell Testing

Details of the cell testing techniques and apparatus have been discussed in earlier reports. (1-4) No changes have been made during the present period, but attempts have been made to standardize cell components. A typical cell assembly now uses pooling type graphite hardware and a high

porosity Kynol matrix. At ERC, cell testing has been standardized at 149°C, the temperature ERC considers to be their baseline temperature for phosphoric acid fuel cells. Fuel cell performance at 160 and 180°C has been measured at UOP. A few cells were tested by ERC using an experimental silicon carbide matrix in place of the Kynol matrix.

IV. RESULTS AND DISCUSSION

4.1 Introduction

In this section, the characteristics and performance of platinum-impregnated Kocite electrodes tested at UOP and ERC are presented. After a discussion, in Section 4.2, of the platinum crystal sintering tests carried out by UOP, the performance of electrodes from various electrocatalyst batches is discussed in Section 4.3. Data on the stability and endurance of cells are presented in Section 4.4. The effects of various fabrication parameters on the optimization of electrode performance are discussed in Section 4.5. In Section 4.6 the results obtained during the third five months of the present contract will be summarized.

4.2 Platinum Particle Sintering Rates

As part of the determination of the stability of Kocite-derived electrocatalysts, initial measurements have been made of the sintering rates of platinum particles on Kocite-derived materials. The results were obtained by X-ray diffraction techniques. After a discussion of the methodology, results are presented for platinum sintering rates of both the electrocatalyst powders and the Kocite electrodes used in operating fuel cells.

The platinum particle agglomeration and size have been determined by the same X-ray diffraction methods previously applied to Kocite electrocatalyst powders. (2) To make this method quantitative for samples having widely differing compositions and thicknesses, cor-

rections have been made for both the change in the X-ray mass absorption coefficients arising from composition variations and the effects of a finite thickness of the sample to X-rays.

Previously the fraction of agglomerated Pt, Ag, was taken as the ratio of the intensity of the diffracted beam for the sample, Is, to the intensity of the diffracted beam for the standard, Ist,

$$Ag = \frac{I_S}{I_{St}}.$$
 (1)

This has been adjusted by dividing the measured intensity, \mathbf{I}_m , by the beam attenuation expected for a certain composition and thickness for both the sample and the standard,

$$I = \frac{I_m}{D \sigma pt} , \qquad (2)$$

where σ pt is the scattering cross-section for platinum and D is the attenuation factor. The standard formulation (5) for D for a sample of variable composition and less than infinite thickness to X-rays is

$$D = \frac{\cos \theta \ CPt}{2 \ \mu_m} \left[1 - \exp\left(\frac{-2 \ \mu_m \ \rho_s}{\cos \theta}\right)\right]$$
 (3)

where θ is the angle between the X-ray beam and the normal to the sample surface, μ_m is the mean mass absorption coefficient for the sample composition, Cp_t is the platinum composition of the sample and ρ_s is the surface density of the catalyst sample in g/cm^2 . (Note that $\rho_s = \rho t$, the density of the material times its thickness.)

E. P. Bertin, <u>Principles and Practice of X-ray Spectrometric Analysis</u>, Plenum Press, New York 1970, pages 416-417.

To estimate the surface area of the platinum particles, they were assumed to be spherical. The agglomerated particles, which the X-ray analysis could measure, were assumed to have the measured mean diameter. The platinum particles with less than 2.0 to 2.5 nm diameter, which are the particles in the unagglomerated fraction, were assumed to have a mean diameter of 2.0 nm. For spherical particles of diameter d (nm) and density ρ (g/cm³), the surface area (6) is

$$SA (m^2/g) = \frac{6000}{d \rho}.$$
 (4)

For 2.0 nm diameter particles, the surface area is $140 \text{ m}^2/\text{g}$. Therefore, the estimated surface area of the samples with the above assumptions of the particle size is,

$$SA = Ag \frac{6000}{d o} + (1-Ag) \cdot 140 \text{ m}^2/\text{g}.$$
 (5)

The sintering results for platinum particles on electrocatalysts are given in Tables 3, 4, and 5. The powders were soaked in 96% H₃PO₄ in pyrex beakers at 180°C for the time indicated. The samples were filtered, washed with deionized water, and dried at 110°C. With samples soaked for 340 and 505 hours, pyrophosphoric acid had formed during the soaking and the filtered samples were washed with caustic to remove it. The Al₂O₃ was assumed to be completely leached for samples soaked for one hour or longer; a fact verified with other samples. The samples soaked for 340 hours were analyzed for their elemental composition and the surface areas of the analyzed samples are indicated in the tables in parentheses. These values are slightly lower than the values for the assumed

In agreement with Exxon Research and Engineering Company, EPRI Catalyst Sintering Program, RF 583-1, Monthly Report #1.

Table III

Platinum Sintering of Kocite Electrocatalyst Powder 3380-104H

X-ray analysis of Pt particle size and surface area for 3380-104H Kocite electrocatalyst powder soaked in $\rm H_3PO_4$ at $180\,^{\circ}C$. The leached electrocatalyst is 12.3 wt.% Pt.

Time (hours)	Particle Size (nm)	Ag (%)	$SA (m^2/g)$
0	6.0	26	116
1	5.9	20	121
24	5.6	28	115
170	6.3	37	105
340	6.5	34	107 (105)
505	5.8	29	113

The number in parenthesis is based on chemical analysis of the sample and should be considered more reliable.

Table IV

Platinum Sintering of Kocite Electrocatalyst Powder 3380-156E

X-ray analysis of Pt particle size and surface area for 3380-156E Kocite electrocatalyst powder soaked in $\rm H_3PO_4$ at $180\,^{\circ}C$. The leached electrocatalyst is 34 wt.% Pt.

Time (hours)	Particle Size (nm)	Ag (%)	$SA (m^2/g)$
0	7.5	31	108
1	6.4	50	92
24	7.3	57	82
170	14.8	100	20
340	14.5	94	(27)

The number in parenthesis is based on chemical analysis of the sample.

Table V

Platinum Sintering on Carbon Black Powder 3310-200E

X-ray analysis of Pt particle size and surface area for 3310-200E carbon black electrocatalyst powder from ERC soaked in $\rm H_3PO_4$ at 180°C. The catalyst is 10 wt.%.

Time (hours)	Particle Size (nm)	Ag (%)	$SA (m^2/g)$
0	4.5	10	132
1	4.3	34	115
24	4.9	42	105
170	5.5	30	113
340	6.5	49	93 (87)

The number in parenthesis is based on chemical analysis of that sample and should be considered as more reliable.

composition and should be considered more accurate. Only traces of phosphate were found in the composition of the samples soaked for 340 hours, indicating that the caustic washing did remove the solid phosphates which had formed.

The sintering results for electrocatalyst powder 3380-104H are given in Table III. The catalyst with 12.3 wt.% platinum in the leached catalyst shows a loss of approximately 10 m²/g in the surface area over the 500 hour test. The results for electrocatalyst 3380-156E, given in Table IV, show a loss of 80 m²/g. The platinum loading of the leached electrocatalyst 3380-156E is 34 wt.% which is three times that of catalyst 3380-104H. For comparison, Table V lists the Pt sintering results for a carbon black based electrocatalyst prepared by ERC. The catalyst with a 10 wt.% platinum loading initially has a higher surface area than the two Kocite-containing powders, but loses 40 m²/g of that surface area, retaining after the sintering test slightly less surface area than electrocatalyst 3380-104.

Tables VI and VII list the results for the sintering of platinum particles in electrodes which were operated in fuel cells. Electrodes are listed by pairs in these tables. The first listing of the pair is for a reference electrode which has not been run in a cell and the second (or third) listing is for the test electrode. The last two pairs of cells listed in Table VI were operated at two different temperatures in succession and this is indicated by the respective slash-separated numbers for temperature and time. For example, the cell with electrode 3380-125B-16 was first operated at 140°C for 425 hours and then at 160°C for 270 hours. The

Table VI

Platinum Sintering Results for Electrodes, 140 to 180°C

Electrodes	Time (hours)	Temperature (°C) ^a	Platinum Concentration $\frac{Pt}{Pt + C}$ (wt.2)	Voltag	Voltage (V) ^b air 02	Particle Size (nm)	Ag (%) e	Surface Area (m²/g)
3380-31B 3380-31B-16	1000	140	18	0.54	0.63	4.9	10.5	130
3380-31K 3380-31K-1	200	140	18	0.52 0.63	0.63	5.4	13 13	129 129
3380-125B 3380-125B-1	820	140	23	0.55 0.62	0.62	6.6	7.4	133
3380-125B 3380-125B-8	475	140	23	0.57	99.0	8.6	17 23	122 113
3380-125B 3380-125B-16	425/270	140/160	23	0.54	0.65	7.0	17 37	123 107
3380-156G 3380-156G-2	100/350	160/180	34	0.63	0.71°	9.8	99	107

^aTwo cells had their operating temperature changed during cell operation. The times indicated refer to intervals at the respective temperatures.

^bIR corrected voltage for the cells operating with the listed electrode as an air or oxygen cathode at 100 ma/cm² at 140°C.

CAt 160°C.

Mean size of crystallites over 2.5 nm diameter.

These results are standardized as discussed in Section 4.2.

Table VII

Platinum Sintering Results for Electrodes, 500 Hours at 180°C

Surface Area (m ² /g)	140	87 85	97	130 108 90
Agglomeration ^C Ag (%)	30	53	43	12 35 49
Particle Size ^b (nm)	7.0	7.0	7.1	4.7 5.8 7.3
Voltages(V)a air 02	1-1	69.0	0.70	0.58
Voltag	1.1	0.61	0.62	0.61
Platinum Concentration $\frac{Pt}{Pt+C} \text{ (wt.2)}$	23 23	34	34 34	999
Temperature (°C)	180	180	180	- 180 180
Time (Hours)	200	200	200	200 200
Electrodes	3289-25F 3289-25F-31	3380-156C 3380-156G-6	3380-156G 3380-156G-8	3310-200C ^d 3310-200C-1 3310-200C-3

 a IR corrected voltages for cells operating with the listed electrode as an air or oxygen cathode at 100 ma/cm² at 140°C.

Mean size of crystallites over 2.5 nm diameter.

^cThese results are standardized as discussed in Section 4.2.

d A set of electrodes containing an ERC Carbon-Black-based electrocatalyst.

voltage listed is the maximum IR corrected voltage for the cell at 100 ma/cm². After the electrodes were run, they were washed in hot deionized water, dried at 110°C, and the catalyst layer removed from the carbon paper backing before the X-ray analysis was made.

Table VI lists the sintering data for electrodes in high performance cells operating mostly at 140°C for various lengths of time. For the cells operated at 140°C, the loss of surface area ranges from 0 to 16 m²/g and stays above 105 m²/g for all samples. The only severe surface area loss measured was with the last electrode pair listed in Table VI. This electrode lost 1/3 of its surface area through operation at 180°C for 350 hours. These data indicate that platinum sintering is probably not a major factor in activity loss for low platinum loaded electrodes at 140°C for periods up to 1000 hours.

Electrodes run in cells for 500 hours at 180°C specifically to study platinum sintering are listed in Table VII. The three carbon black electrodes (3310-200C series) were obtained from ERC. The 3289-25F and 3310-200C electrode sets show loses ranging from 20 to 40 m²/g. Data obtained with the 3380-156G electrode sets are contradictory, with one electrode showing no loss in surface area and the other having a 50% loss of surface area. The zero loss result may be an experimental artifact, however the surface area loss for the other 3380-156G electrode is still not as severe as the surface area loss for the 3380-156E powder sample. No drop in cell performance due to the loss in the platinum surface area was observed in the electrode lifetime tests for the 3380-156G electrodes.

4.3 Fuel Cell Performance Results

4.3.1 Introduction

In this section the performance results for cells tested during the third five month period of the contract will be presented. Lifetime test data will be discussed in Section 4.4 and the analysis of the cell performances as they bear on the optimization of the electrodes will be given in Section 4.5. The fuel cell design and testing procedures have been discussed in Section 3.

The characteristics of the Kocite electrodes and cell builds tested at ERC and UOP are listed in Tables VIII and IX respectively. The cells included in the review of previous results in Section 1.3 have also been listed in these tables. Cell build characteristics are given for cells that performed well or that are otherwise noteworthy. In most cases the electrodes had a nominal platinum loading of either 0.25 or 0.5 mg/cm2. Electrodes fabricated from electrocatalyst batch 3380-156G having a 0.25 mg/cm2 platinum loading and the electrodes from electrocatalyst batch 3380-180F had half the normal catalyst loading of 5 mg/cm2. The teflon content was varied from 18 to 50 wt.% with most electrodes having a teflon content of 20 or 30 wt.% relative to the Kocite loading prior to leaching. Almost all electrodes fabricated during this period were machine-rolled with medium catalyst layer densities. The exceptions are the low teflon content electrodes of catalyst batches tested previously which were made in small quantities for preliminary testing by ERC. All ERC cells and most UOP cells are operated with an electrolyte pool in the cell hardware to

Table VIII

Times a

Characteristics of Pt-Doped Kocite Electrodes - ERC

Teflon Content After Nominal Leaching Fabrication (wt.%) (wt.%) Method	Machine 65 Machine	0 70 Machine 0 78 Machine	0 61 Machine 0 61 Machine	0 61 Machine	97	30 53 Machine	97		20 46 Machine	97		18 50 Hand	20 46 Machine
Platinum Concentration Pt Pt + C (wt.%)	21 22 3	35 35 5	35	35 3	35 2	53 3	35 2	35 3	35 2			21 1	35 2
Platinum st Loading (mg/cm ²)		6G 0.26 6G 0.28	6G 0.26 6G 0.56	.,	(3	G. 6	566 0.54		566 0.54		SF 0.47	125B 0.48	1566 0.54
Kocite Electrocatalyst Batch	3380-1251 3380-1251	380-15 380-15	3380-156G 3380-156G	380-15	380-1	3380-180	380-180F	3380-156	380-1	380-1	289-2	380-125	3380-156G

^aMedium bonding pressure = 100 psi.

Table IX

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Characteristics of Pt-Doped Kocite Electrodes - UOP

		Platinum	Teflon	Teflon Content			Relative	
	Platinum	Concentration		After		Test Hardware	Catalyst	
Cell Build No.	(mg/cm ²)	Pt + C (wt. %)	(wt.%)	(wt.%)	Method	and Electrode Substrate	Density	Prevetted
3173-1736-10	0.24	13	30	65	Hand-Rolled	Tantalum	High	1 hour
3173-1730-16	0.24	13	30	65	Hand	Tantalum	High	1 hour
3289-25F-24	0.50	23	30	20	Hand	Graphite Pooling	High	1 day
3289-25F-30	0.50	23	30	20	Hand	Tantalum	High	1 day
3380-31B-10	0.25	11	30	61	Hand	Graphite	High	1 hour
3380-125B-21	0.22	21	30	65	Machine	Graphite	Medium	1 day
3380-125B-24	0.22	21	30	65	Machine	Graphite	Medium	1 day
3380-125B-25	0.22	21	30	65	Machine	Graphite	Medium	1 day
3380-125B-26	0.24	21	20	52	Machine	Graphite	Medium	1 day
3380-125B-28	0.24	21	70	52	Machine	Graphite	Medium	1 day
3380-1566-1	0.26	35	07	02	Machine	Graphite	Medium	None
3380-156G-2	0.26	35	40	70	Machine	Graphite Pooling	Medium	1 day
3380-156G-4	0.26	35	07	20	Machine	Graphite	Medium	1 day
3380-156G-7	0.56	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-1566-8	0.56	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-1566-9	0.56	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-156G-11	0.56	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-1566-13	0.54	35	20	94	Machine	Graphite Pooling	Medium	1 day
3380-156G-14	0.54	35	20	94	Machine	Graphite Pooling	Medium	1 day
3380-156G-15	0.54	35	20	97	Machine	Graphite Pooling	Medium	1 day
3380-156G-16	0.54	35	70	94	Machine	Graphite Pooling	Medium	1 day

Bonding pressure - High = 2000 psi, Medium = 100 psi.

Table IX (Cont'd)

Posterior A

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Characteristics of Pt-Doped Kocite Electrodes - UOP

		Platinum	Teflon Content	Content			Relative	
Cell Build No.	Platinum Loading (mg/cm ²)	P P	Nominal (wt.%)	After Leaching (wt.%)	Fabrication Method	Test Hardware and Electrode Substrate	Catalyst Layer Density	Electrode
3380-1566-17	0.58	35	20	97	Machine	Graphite	Medium	1 day
3380-1566-18	0.58	35	20	94	Machine	Graphite Pooling	Medium	1 day
3380-156G-19	0.42	35	30	61	Machine	Graphite Pooling	Medium	1 day
3380-156G-21	0.54	35	20	94	Machine	Graphite Pooling	Medium	1 day
3380-156G-22	0.58	35	20	94	Machine	Graphite	Medium	l day
3380-1566-23	0.58	25	20	94	Machine	Graphite Pooling	Medium	2 days

Bonding pressure - High * 2000 psi, Medium = 100 psi.

improve lifetime performance by preventing matrix dryout. Prewetting of the Kocite electrodes by float filling in H₃PO₄ at 140°C was continued because cells assembled dry tended to develop gas crossover. All cells were assembled using an ERC fabricated 2 mg/cm² Pt black electrode as the counter electrode except for cell 3380-156G-23 which had Kocite electrodes for both the anode and cathode.

The performance levels of the cells listed in Tables VIII and IX are summarized in Tables X and XI, respectively. In these tables the full cell terminal and IR corrected voltages at 100 ma/cm² are listed for cells with the Kocite electrode used as an air cathode, oxygen cathode, and hydrogen (vs. standard air) anode. Fuel cell operation was normally conducted at 150°C at ERC and 160 and 180°C at UOP. Also listed in Tables X and XI is the oxygen gain number for each cell. ERC did not report resistance corrections for individual cells, so a ~40 mV correction at 100 ma/cm² has been assumed. This correction is consistent with corrections measured at UOP, and previous ERC experience. In general, comparable performance levels have been measured at ERC and UOP on cells with electrodes from the same electrode batch.

The highest performance level obtained by ERC was with cell SiC-3 having a silicon carbide matrix and a cathode from electrocatalyst batch 3380-156G loaded with 0.54 mg/cm² platinum. At 180°C it produced 0.66 V terminal operating on air and 0.73 V terminal on oxygen at 100 ma/cm² as shown in Figure 5. The highest performance

Table X

1

Summary of ERC Cell Performance Results

		المة	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
		C C E	15	15	150	15	15	18	15	15	150	18	15	15	18	15	15	150	15	15	180
	02	Gain (mV) ^d	110	8	20	8	80	20	8	8	80	8	8	100	100	100	80	8	140	90	02
/cm² with	IR Corrected Voltage	H ₂ (vs air)	0.58	0.63	09.0	0.64	99.0		0.65	0.64	0.67	99.0	09.0	9.0	0.65	0.67	0.67	9.0	0.64	0.64	1
100 ma e On	orrect	05	9.0	99.0	09.0	0.68	0.72	0.73	99.0	0.71	0.70	69.0	99.0	0.70	0.71	69.0	0.70	0.70	99.0	69.0	0.77
s) at ectrod	IR C	Air	0.53	0.58	0.53	0.60	0.64	99.0	0.58	0.63	0.62	0.60	0.57	0.60	0.61	0.59	0.62	0.61	0.52	09.0	0.70
Cell Voltages ^a (volts) at 100 ma/cm² with Kocite Electrode On	Voltage	H ₂ (vs air)	0.54	0.59	0.56	09.0	0.62	•	0.61	09.0	0.63	09.0	09.0	09.0	0.61	0.63	0.63	09.0	09.0	09.0	1
e11 Vo	Terminal	03	09.0	0.62	0.56	9.0	99.0	69.0	0.62	0.67	99.0	0.65	0.62	99.0	0.67	0.65	99.0	99.0	0.62	9.0	0.73
O	Te	Air	0.49	0.54	0.49	0.56	0.60	0.62	0.54	0.59	0.58	0.56	0.53	0.56	0.56	0.55	0.58	0.56	0.48	0.56	99.0
	Teflon	[wt.%]			50 (78)		_			20 (46)			(99) 07	20 (46)			1	20 (46)		ETC.	20 (46)
		Loading L (mg/cm ²)	0.22	0.26	0.28	0.26	0.56			0.54				0.54		0.42	0.54	0.58	0.47	0.48	0.54
		Kocite	3380-125B	3380-1566	3380-1566	3380-1566	3380-1566		3380-1566	3380-1566	3380-180F		3380-180F	3380-1566		3380-1566	3380-1566	3380-1566	3289-25F	3380-125B	3380-1566
		Cell Build Number			ERC 86					ERC 95			ERC 97	ERC 99		ERC 100	ERC 101	ERC 102	ERC 105	ERC 107	S1C-3

aCell voltage obtained with a 2 mg/cm2 Pt-black counter electrode.

Nominal teflon loading - figures in parenthesis are values for the leached electrodes.

Measured at the current collector plates.

Though no resistance correction has been reported by ERC, a 40 mV IR correction has been assumed for consistancy with the UOP data.

evoltage difference between air and oxygen performance at 100 ma/cm2.

Table XI

Summary of UOP Cell Performance Results

		é		8	11 Volt	ages (v	Cell Voltages (volts) at 100 ma/cm ² with Kocite Electrode On	100 ma/c	m ²	ć	
Cell Build	Loading	Loa	cading	Termina	1 Volta	Terminal Voltage (V)	IR Conn	IR Connected Voltage	ltage (V) ^d	Gaine	Temperature
Number	HB/CH	4	WE. 6/	ALL	5	H2	AL.	2	H 2	(III)	
3380-125B-21	0.22	3	30 (65)	0.43	0.55	0.53	0.54	99.0	0.64	120	140
				0.51	09.0	09.0	0.59	0.68	89.0	06	160
3380-125B-24	0.22	8	(65)	0.47	0.58	0.58	0.57	0.68	0.68	110	160
3380-125B-25	0.22	8	_	0.52	0.63	0.59	0.61	69.0	0.65	80	160
3380-125B-26	0.24	20	(25)	0.55	89.0	0.64	0.59	0.71	0.67	120	160
				0.57	0.67		0.62	0.72		100	180
3380-125B-28	0.24	20	(42)	0.56	0.65		0.61	69.0	•	80	160
				09.0	0.67	•	0.63	0.70	•	02	180
3380-156G-1	0.26	9	_	0.54	0.61	0.55	0.58	0.71	0.65	130	160
3380-1566-2	0.26	40	(02)	0.58	99.0	0.65	0.63	0.71	69.0	80	160
				0.59	99.0	0.65	0.62	69.0	89.0	20	180
3380-1566-4	0.26	40	(00)	0.54	9.0	0.63	0.59	69.0	89.0	100	160
				0.59	99.0	0.64	0.63	0.70	89.0	20	180
3380-1566-7	0.56	3	_	0.57	99.0	0.59	09.0	0.69	0.62	06	160
3380-156G-8	0.56	30	(61)	0.58	89.0	0.67	0.62	0.72	0.71	100	160
				0.58	99.0	•	0.62	0.70		80	180

*Nominal teflon loading - figures in parentheses are values for the leach electrodes.

^bCell voltage obtained with a 2 mg/cm² Pt black counter electrode (see f) for cell 3380-156G-23.

Measured at the current collector plates.

Resistance measured with a 1 KHz Resistance Bridge.

evoltage difference between air and oxygen performance at 100 ma/cm².

The cell had Kocite electrodes as both the anode and cathode.

Table XI (Cont'd)

7

Summary of UOP Cell Performance Results

				ŏ	ell Volt	Cell Voltages ^D (volts) at 100 ma/cm ²	olts) at	100 ma/	cm ²		
	Platinum	Tef	Teflon		wit	with Kocite Electrode On	Electro	de On		0	
Cell Build	Loading	Load	oading	Termin	Ferminal Voltage (V) ^C		IR Conne	IR Connected Voltage	tage (V) ^d	Gaine	Temperature
Number	(mg/cm^2)	3	(wt. %)	Air	02	•	Air	02	H ₂	(mV)	0.
3380-1566-9	0.56	30	30 (61)	0.58	0.67	0.52	0.61	0.70	0.55	06	160
				0.61	69.0	0.59	0.64	0.72	0.62	80	180
3380-1566-11	0.56	30	(61)	0.61	89.0	0.70	0.63	0.70	0.72	20	160
				0.63	69.0	0.63	99.0	0.72	99.0	09	180
3380-1566-13	0.54	20	20 (46)	0.61	69.0	0.64	0.64	0.72	0.68	8	160
				0.62	0.70	99.0	0.65	0.73	69.0	80	180
3380-1566-14	0.54	70	(94)	09.0	69.0	0.62	0.64	0.72	0.65	06	160
				0.62	69.0	99.0	99.0	0.74	89.0	02	180
3380-1566-15	0.54	20	(99)	0.61	0.70	0.67	0.65	0.74	0.67	06	160
				0.62	0.70	99.0	99.0	0.74	0.70	88	180
3380-1566-16	0.54	20	(46)	0.52	0.59	0.52	0.65	0.72	79.0	2	160
3380-1566-17	0.58	20	(94)	0.59	0.68	0.63	0.63	0.72	99.0	06	160
3380-1566-18	0.58	70	(97)	0.56	99.0	09.0	09.0	0.70	0.65	100	160
3380-1566-19	0.42	8	(61)	79.0	0.70	0.63	19.0	0.73	0.65	09	160
				0.65	0.71	0.65	89.0	0.74	19.0	09	180
3380-1566-21	0.54	20	(97)	0.61	0.70	0.65	0.65	0.72	0.67	06	160
				0.63	0.70	19.0	0.67	0.74	0.71	20	180
3380-1566-22	0.58	20	(46)	0.56	99.0	0.62	09.0	0.70	99.0	100	160
3380-156c-23 ¹	0.58	20	(94)	0.56	9.0	1	0.63	0.70	•	02	160
				0.57	9.0	•	0.63	0.70	•	20	160

Nominal teflon loading - figures in parentheses are values for the leached electrodes.

bcell voltage obtained with a 2 mg/cm2 Pt black counter electrode (see f) for cell 3380-156G-23.

GMeasured at the current collector plates.

desistance measured with a 1 KHz Resistance Bridge.

evoltage difference between air and oxygen performance at 100 ma/cm².

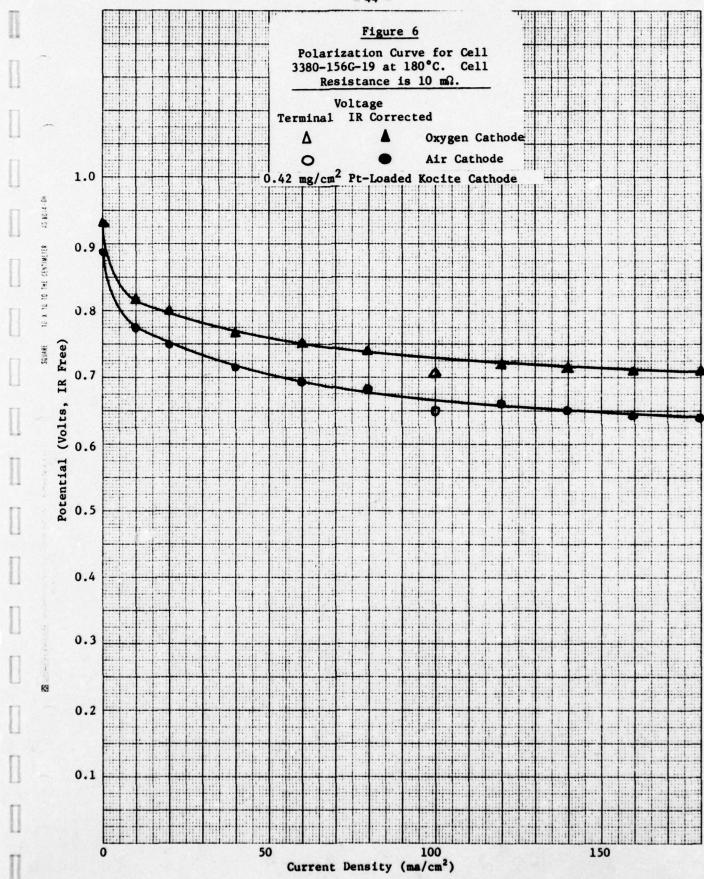
The cell had Kocite electrodes as both the anode and cathode.

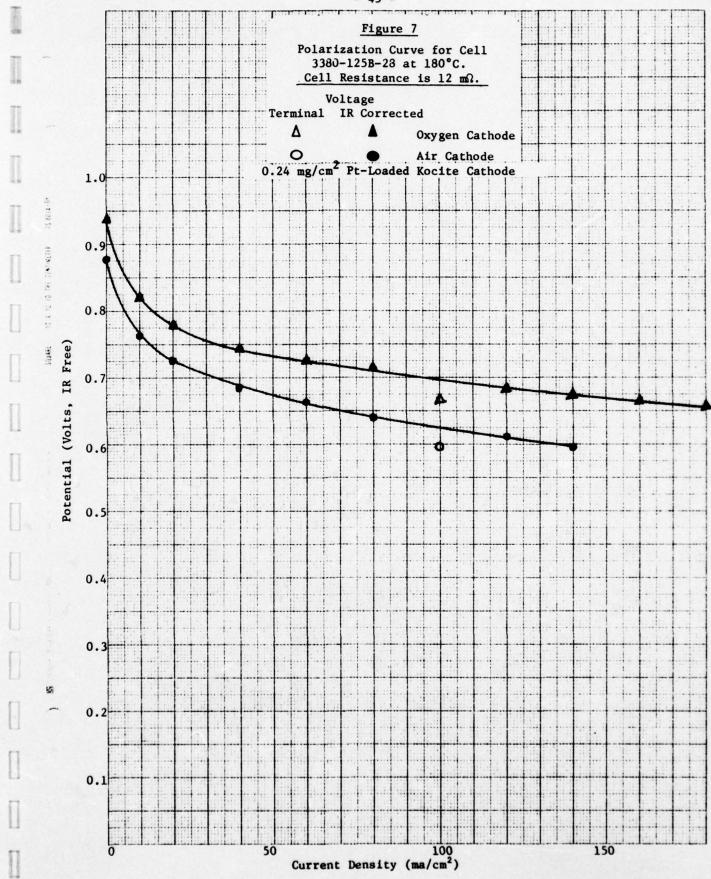
of a cell with a Kynol matrix was achieved by the UOP cell shown in Figure 6 with a 0.42 mg/cm² Pt loading. This cell operated at 0.65 V terminal on air and 0.71 V terminal on oxygen at 180°C and 100 ma/cm².

4.3.2 Kocite Electrocatalyst Batch 3380-125B Pt Loading 0.125 to 0.25 mg/cm²

The performance of the majority of the cells built with electrodes containing this catalyst were reported in detail in the previous Interim Report. (4) This was the first large electrocatalyst batch from which machine calendered electrodes were fabricated. Details of the results obtained by varying the structure of the electrodes prepared from this batch are discussed in that report. (4) Testing has been completed during this period on two electrode batches prepared from this electrocatalyst batch, one with loadings of 0.22 mg/cm² Pt and 30 wt.% teflon and the other with 0.25 mg/cm² Pt and 20 wt.% teflon. Cells with electrodes from these batches performed better than cells with electrodes from other electrode batches fabricated from the 3380-125B electrocatalyst. These electrodes, along with an electrode fabricated from the 3380-156G electrocatalyst batch, to be discussed in Section 4.3.3, gave the best performance of any Kocite-containing electrodes to date having a platinum loading of ~0.25 mg/cm².

Figure 7 shows the full cell polarization curves for the best cell of this group. At 180° C, the cell produced IR corrected voltages of 0.63 V when operated on air and 0.70 V on oxygen at 100 ma/cm². The best cell using an electrode from the other electrode





batch was shown in Figure 4 and was reported in the previous Interim Report. (4) Table XII contains a summary of the performance of cells containing electrodes from these two electrode batches. (ERC Cell 83 was started with no float filling and never attained the level of performance achieved by the other cells.) The rest of the cells had an oxygen performance that was comparable, with a variation in the O₂ gain at 100 ma/cm² of between 70 and 110 mV.

4.3.3 Kocite Electrocatalyst Batch 3380-156G Pt Loading 0.26 to 0.58 mg/cm²

Electrodes fabricated from electrocatalyst batch 3380-156G produced the highest performance levels of any electrodes tested during this program. The best full cell polarization curves for a cell containing an electrode incorporating this electrocatalyst batch, with a Kynol matrix, are shown in Figure 6. At 180°C and with a 0.42 mg/cm² Pt-loaded electrode, this cell maintained IR corrected voltages of 0.67 V when operated on air and 0.73 V on oxygen at 100 ma/cm². The internal resistance of the cell was very low, with the terminal voltages being 0.65 V on air and 0.71 V on oxygen. Comparable performance was obtained with another cell as shown in Figure 8. This second cell, with an electrode having a platinum loading of 0.54 mg/cm², had IR corrected voltages of 0.66 on air and 0.73 on oxygen at 100 ma/cm².

Table XII

Summary of Best Performance for Electrodes from Electrocatalyst Batch 3380-125B

 Cells 3380-125B-21, 24, 25 and ERC 75 and 83

 0.22 mg/cm² Pt
 30 wt.% Teflon

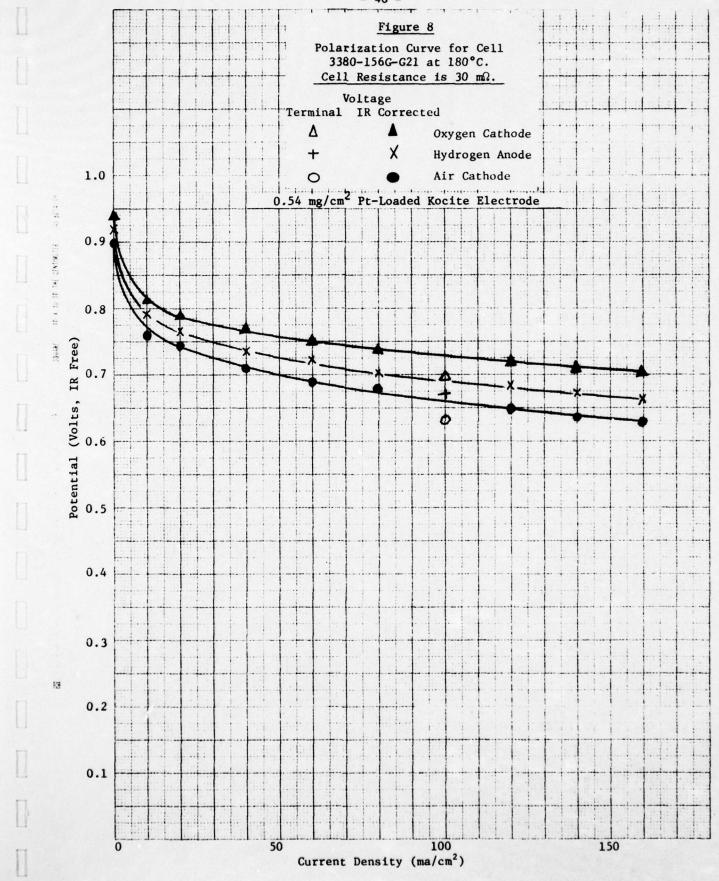
Voltage (V) at 100 ma/cm²

	Teri	minal	I	R Corrected	
Cell_	Air	<u>Oxygen</u>	Air	O ₂ Cathode (V)	Temperature (°C)
UOP 21	0.51	0.60	0.59	0.68	160
UOP 24	0.47	0.58	0.57	0.68	160
UOP 25	0.52	0.63	0.61	0.69	160
ERC 75	0.56	0.65	0.62	0.71	150
ERC 83	0.49	0.60	0.53	0.64	150

Cells 3380-125B-26 and 28 and ERC 89 0.24 mg/cm² Pt 20 wt.% Teflon

Voltage (V) at 100 ma/cm²

	Ter	minal	I	R Corrected	
Cell	Air	Oxygen	Air	O2 Cathode (V)	Temperature (°C)
UOP 26	0.57	0.67	0.62	0.70	180
UOP 28	0.60	0.67	0.63	0.70	180
ERC 82	0.54	0.62	0.57	0.67	150



Electrodes fabricated from electrocatalyst batch 3380-156G were run in cells operated under the same conditions to determine the reproducibility of performance within an electrode batch. Table XIII tabulates the air cathode, oxygen cathode and hydrogen anode (vs. standard air) results at 160°C for electrodes from three different electrode batches prepared with slightly different fabrication techniques. In each case the performance of three or more electrodes was determined. Though large spreads occur in the terminal voltages due to differing cell resistances, the values of the IR corrected voltages are close. For Set 1, the IR corrected air cathode values differ by 19 mV and the oxygen cathode values by 23 mV. For Set 2, the air cathode voltages vary by only 11 mV and the oxygen cathode values by 18 mV. For Set 3, the air cathode differences are 33 mV and the oxygen cathode differences are 20 mV. The oxygen gain values at 100 ma/cm² differ by 10 to 20 mV among the sets. The most reproducible performance levels were obtained using electrodes in Set 2. More electrodes from this batch were tested and in each case where the cell performed well, the cell voltage was within a few mV's of its peak value in 24 hours. The results achieved using the Set 2 electrodes indicate that reproducible performance should be obtainable using Kocite electrodes.

A few of the 0.54 mg/cm² Pt-loaded electrodes were tested by ERC with an experimental SiC matrix rather than the usual Kynol matrix. While several of these cells had gas crossover problems, the performance of cell SiC-3, shown in Figure 5, is about 40 mV higher than

Table XIII

Summary of UOP Results

Cell Performance and Reliability

Electrodes from Electrocatalyst Batch 3380-156G - 160°C Voltage (mV) at 100 ma/cm²

Set 1 - 30 wt.% PTFE, medium density, 0.56 mg/cm2 Pt loading

	Air Cathode		0 ₂ Cathode		O ₂ Gain	H ₂ Anode	
Cell	Term	IRC	Term	IRC		Term	IRC
7	570	605	656	691	86	585	620
8	582	617	679	714	97	675	710
9	583	615	675	700	92	523	555
11	609	624	687	703	78	703	720

Set 2 - 20 wt.% PTFE, medium density, 0.54 mg/cm2 Pt loading

	Air Cathode		0 ₂ Cathode		O ₂ Gain	H ₂ Anode	
Cell	Term	IRC	Term	IRC		Term	IRC
13	614	646	688	717	74	650	680
14	602	638	688	721	86	622	655
15	609	645	698	735	89	673	670
16	523	649	592	718	69	517	643
21	614	643	700	741	93	653	668

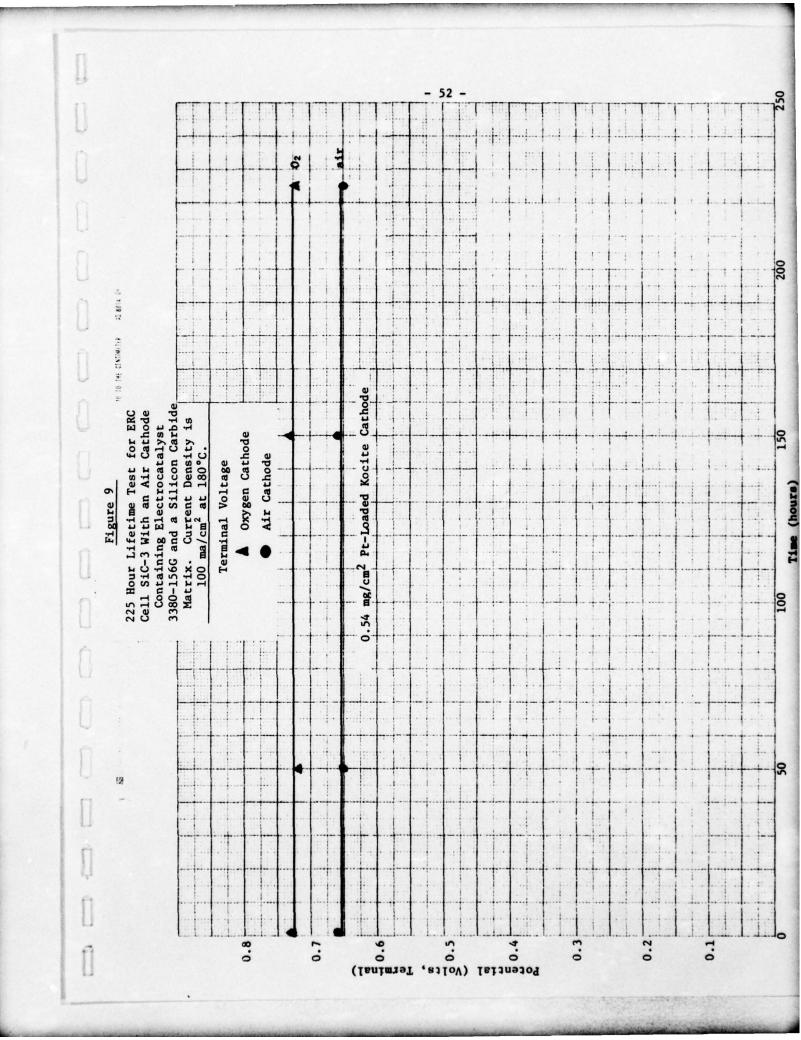
Set 3 - 20 wt.% PTFE, medium density, 0.58 mg/cm² Pt loading

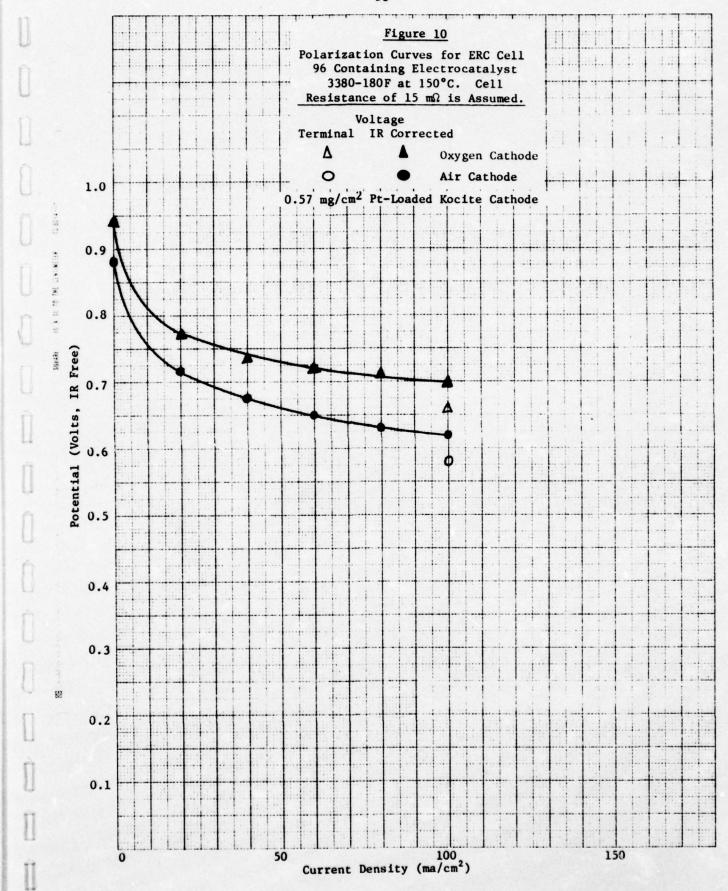
	Air Cathode		O ₂ Cathode		O ₂ Gain	H ₂ Anode	
Cell	Term	IRC	Term	IRC		Term	IRC
17	592	631	682	716	90	630	663
18	558	598	657	696	99	602	645
22	557	600	657	699	100	616	655

ERC obtained with the same type of electrode using a Kynol matrix. The reason for the performance increase is not known, however the internal resistance is not substantially different for the cells, indicating that the increase is not an internal resistance effect. The primary value of the SiC matrix is that it will allow operation at 180°C and above without a matrix degradation problem. The 225 hour life test shown in Figure 9 shows the basic stability of the cell, however gas crossover in the matrix occurred at that time. Further development of the matrix should improve cell life.

4.3.4 Kocite Electrocatalyst Batch 3380-180F Pt Loading 0.33 to 0.57 mg/cm²

This batch was impregnated at a level of 20 wt.% based on the Kocite base material. After leaching, the platinum concentration is 52 wt.% based on the remaining carbonaceous pyropolymer. Because of this high platinum concentration, the platinum particle size and agglomeration listed in Table 2, are high. Because of the large platinum particle size, testing of this electrocatalyst was limited. The performance of a cell containing this electrocatalyst is shown in Figure 10 and is not as good as that for the cells containing electrodes from electrocatalyst batch 3380-156G having a similar Pt-loading. The high platinum agglomeration of this batch makes it difficult to compare results obtained using electrodes from other electrocatalyst batches because the platinum particle size distribution differs substantially from that of other batches.

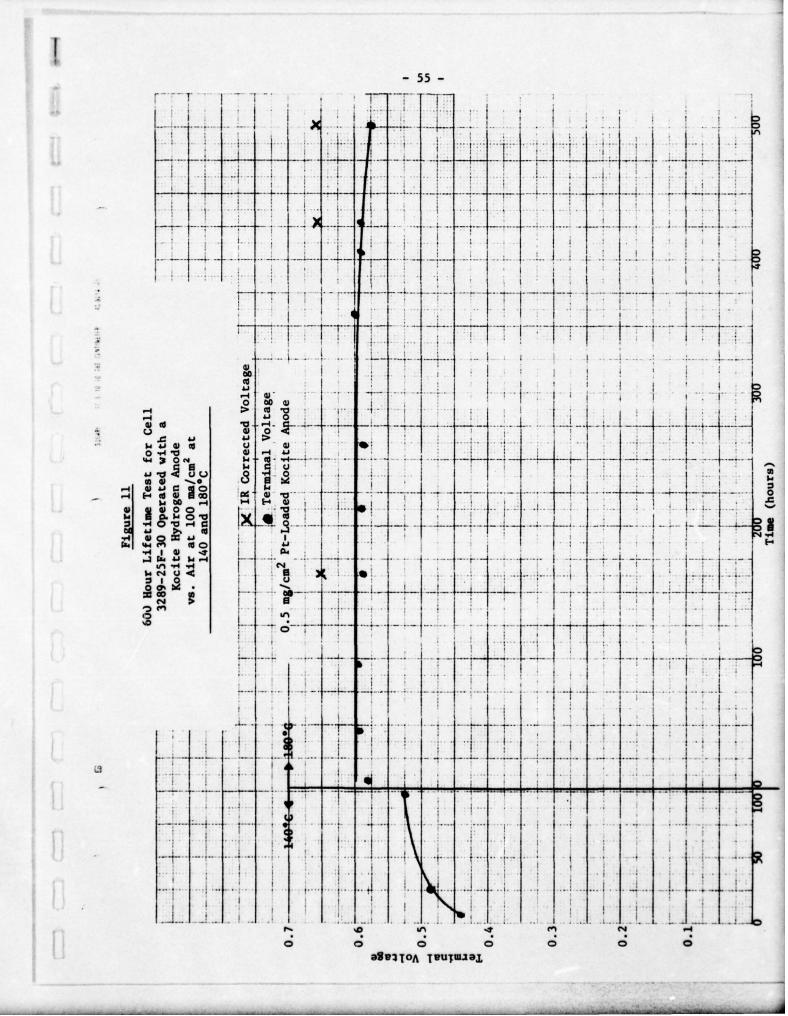




4.3.5 Anode Performance and CO Tolerance

The emphasis during this contract has been on evaluating the cathode performance rather than the anode performance of Kocite electrodes. The best voltage obtained for a cell with a Kocite anode is a terminal value of 0.70 V at 100 ma/cm² and 160°C. The anode polarization of a cell is low compared with the cathode polarization, so that this terminal voltage is more indicative of a good cathode performance by the platinum black electrode rather than a superior anode performance by the Kocite electrode. The variation of anode results listed in Tables X and XI further suggests that the values may depend more on the platinum black cathode than the Kocite anode. Three areas of a ode performance are discussed below, (A) anode lifetime tests, (B) CO tolerance of Kocite electrodes, and (C) use of Kocite electrodes as both the anode and cathode in a cell.

(A) The ability of Kocite anodes to operate stably was shown in the previous Interim Report (4) for the cell shown in Figure 11. Though the terminal voltage began to drop after 300 hours of operation at 180°C, this drop was due to increased cell resistance and the IR corrected voltage remained fixed at 0.66 V at 100 ma/cm². Another example of this stability is displayed in Figure 12 by the lifetime test for cell 3380-156G-23 with both a Kocite anode and cathode. Though the terminal voltage at 160°C and 100 ma/cm² has decreased 30 mV in 1200 hours, the IR corrected voltage has been



0.625 ± 0.005 V over that time. Since the IR corrected voltage is comparable to other cells with the same cathode and 2 mg/cm² platinum black anodes, listed in Table XIII, these data indicate that the anode as well as the cathode gives stable performance at 160°C for over 1200 hours.

(B) Initial data are available on the short term resistance of Kocite anodes to CO poisoning. Two cells were tested with a mixture of 5% CO in the H2 fuel gas. The results for 5 to 10 minute exposures for the Kocite anodes and the 2 mg/cm2 Pt black anodes are shown in Table XIV. The cell listed first had been operated for 1700 hours at 160°C while the cell listed second had been operated for 800 hours at 160°C and 1000 hours at 180°C. The values given in the table are the voltage changes of the cell on switching from pure H2 to the CO-H2 mixture for 5 minutes. In the first cell, the Kocite electrode shows only half the change at 180°C that the Pt black electrode does. For the second cell, the Kocite electrode has 1/5 the change that the Pt black electrode has. At lower temperatures the performance differential favors the Kocite electrode even more noticeably. The poor performance of the second cell using the Pt black electrode may be due to sintering of the platinum in the Pt black electrode at 180°C. Though more deterioration could be expected for longer exposures to the CO, the short term resistance of the Kocite electrodes compared to Pt black electrodes is very good.

Table XIV

CO Tolerance of Anodes

Cell 3380-156G-19

	Voltage Difference (mV)				
	Kocite Anode	Pt-Black Anode			
180°C	5	10			
160°C	6	20			

Cell 3380-156G-11

	Voltage Difference (mV)				
	Kocite Anode	Pt-Black Anodeb			
180°C	5	25			
160°C	8	60°			
140°C	25	300 ^d			

 $^{^{\}mathbf{a}}$ Voltage difference between the cell operating on pure H_2 and a 5% CO- H_2 mixture for 5 minutes.

^bCommercial 2 mg/cm² Pt-black electrodes used as counter electrodes in all test cells.

 $^{^{\}rm C}$ Initial decline was $^{\rm C}$ 3 mV/min, continued for $^{\rm C}$ 30 min.

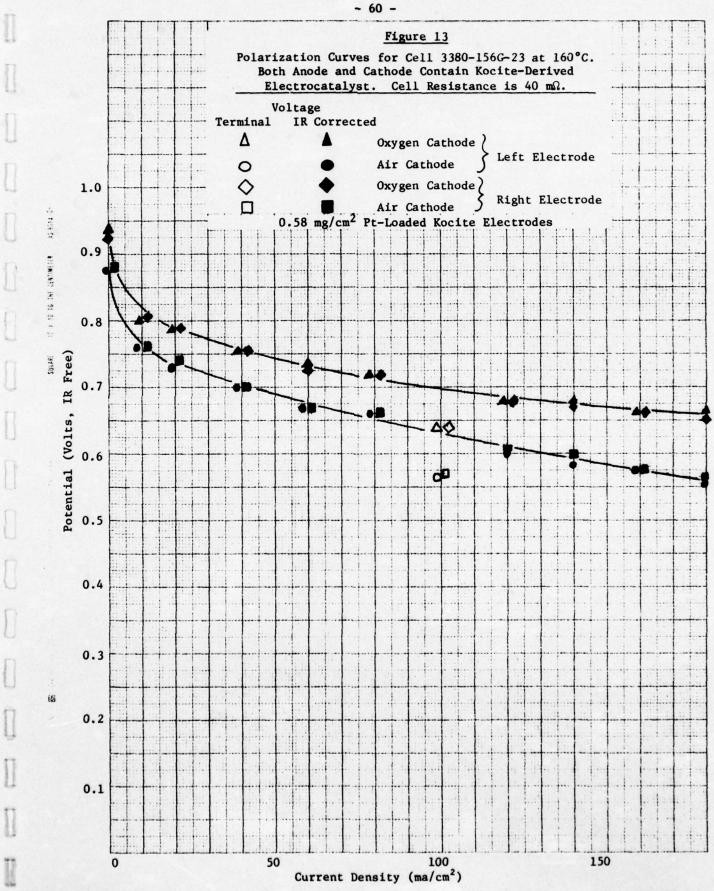
 $^{^{\}rm d}$ Initial decline was $^{\sim}100$ mV/min, eventually declined by >400 mV.

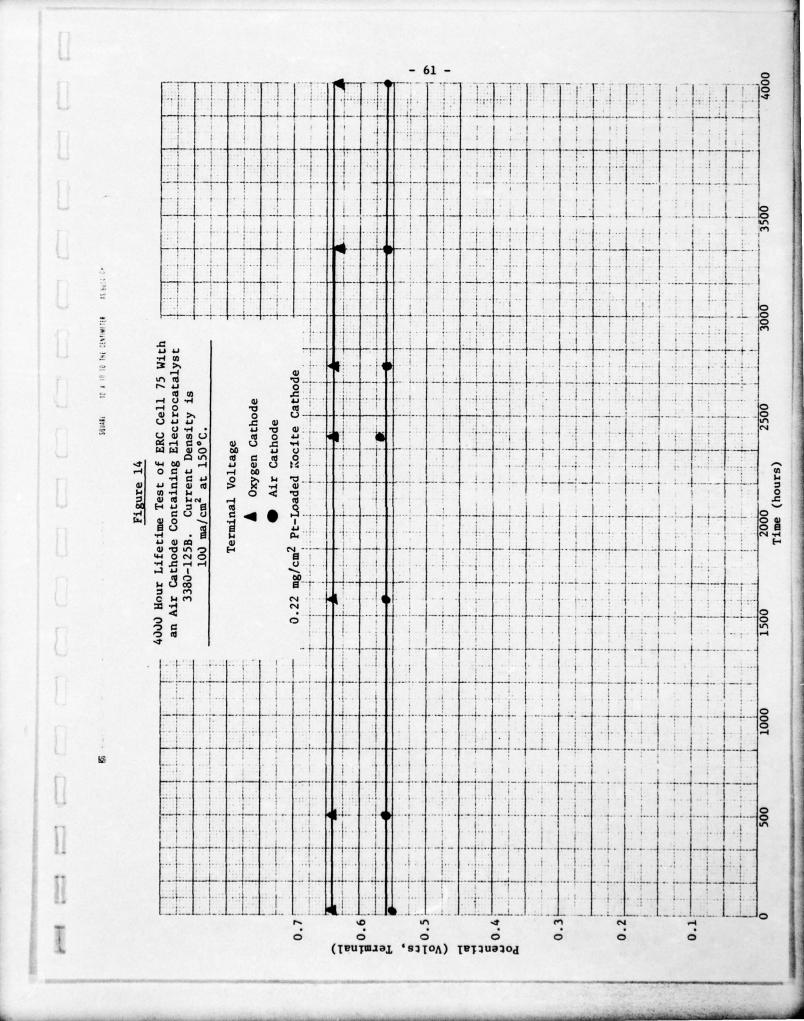
(C) UOP Cell 3380-156G-23 is the first cell assembled with both a Kocite cathode and anode in the same cell. The performance compares quite well with the other Set 3 group of cells in Table XIII, which have the same electrode for a cathode. Figure 13 shows the polarization curve for the cell. As shown in this figure, the curves for the cell with the anode and cathode electrodes reversed is superimposable on the curves shown. The IR corrected voltages with either direction of gas flow were 0.62 V on air and 0.70 V on oxygen at 160°C and 100 ma/cm². These data indicate that with pure H₂, the polarization contributed by Kocite anodes is not significantly greater than that of the standard 2 mg/cm² platinum black anodes.

4.4 Electrode Lifetime Tests

Although only 500 hour tests were required by the contract, substantial efforts have been made to determine the longer term performance of cells with Kocite electrodes. Cells with these electrodes are stable with no loss in the IR corrected performance over periods of several thousand hours at temperatures up to 180°C. The use of graphite cell hardware with an electrolyte reservoir has helped minimize cell dryout and stabilize the terminal voltage performance of the cells.

As an example of the stability of cells with Kocite electrodes used as air cathodes, cell ERC 75 was still operating at 150°C after 4000 hours of operation (6 months). In this case an electrode from electrocatalyst batch 3380-125B was used. As shown in Figure 14,

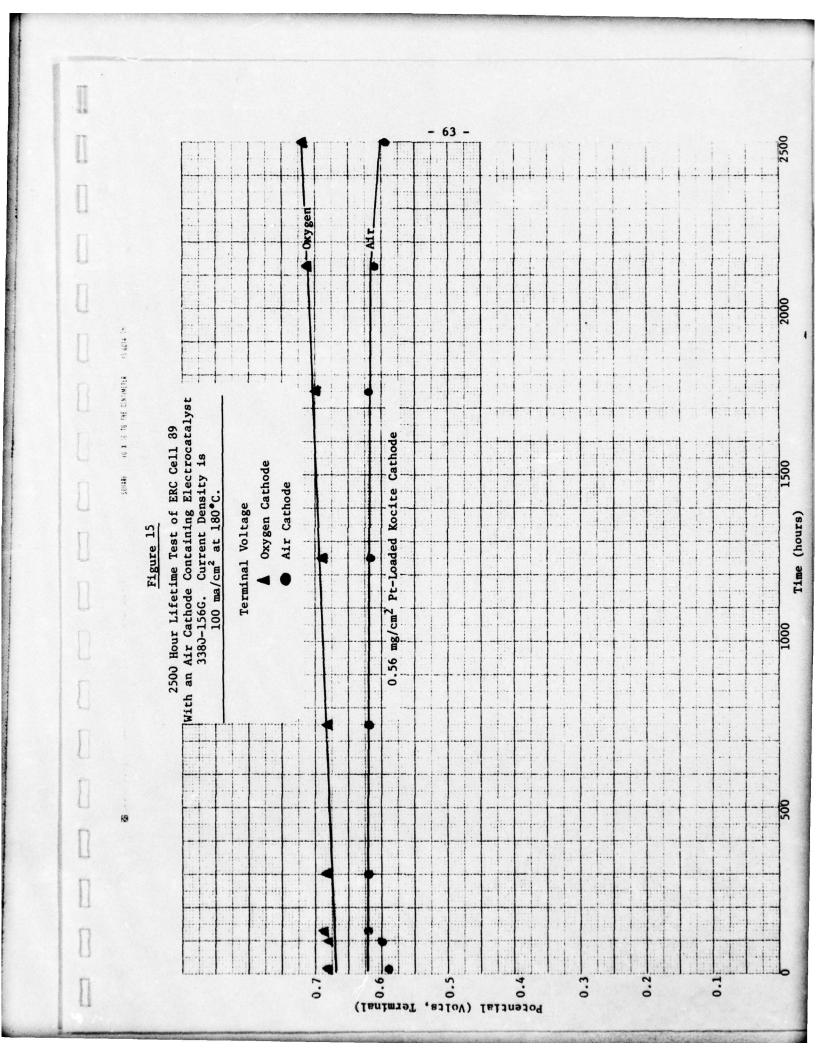




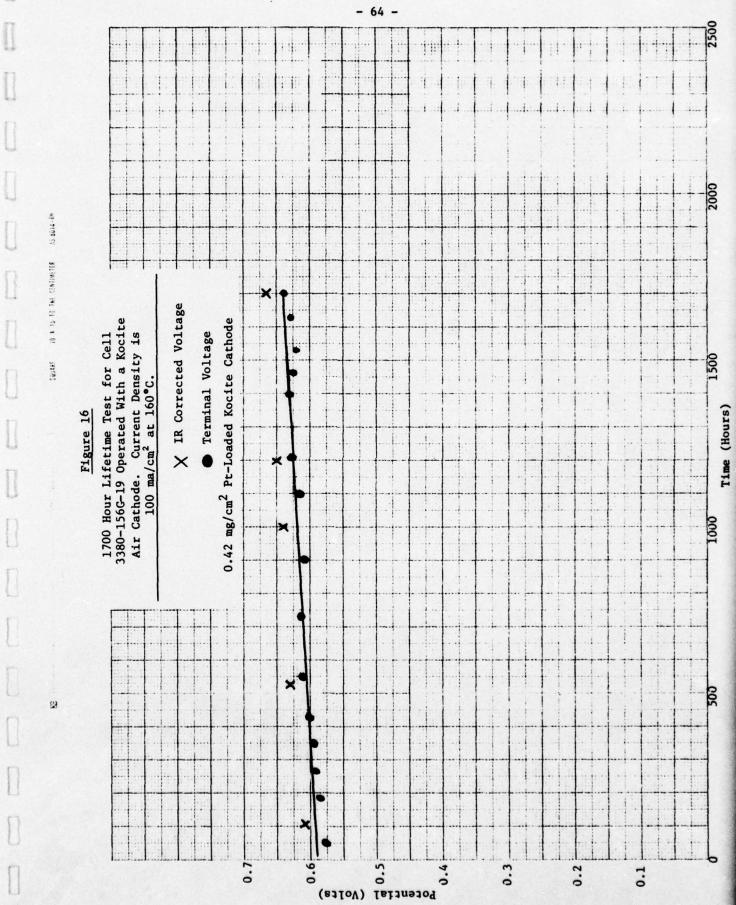
the terminal voltage of the cell at 100 ma/cm² has been stable at 0.56 V. At 180°C, a cell with a cathode made from electrocatalyst batch 3380-156G has had increasing oxygen cathode performance for over 2500 hours, as shown in Figure 15. At 100 ma/cm² and 180°C, the terminal voltage of the cell on oxygen reached 0.72 V, while on air the cell voltage dropped below 0.60 V, giving an oxygen gain of 120 mV. This indicates the growth of some diffusion related loss, possibly catalyst layer flooding. No resistance corrections are available for these cells to allow evaluation of the IR corrected performance.

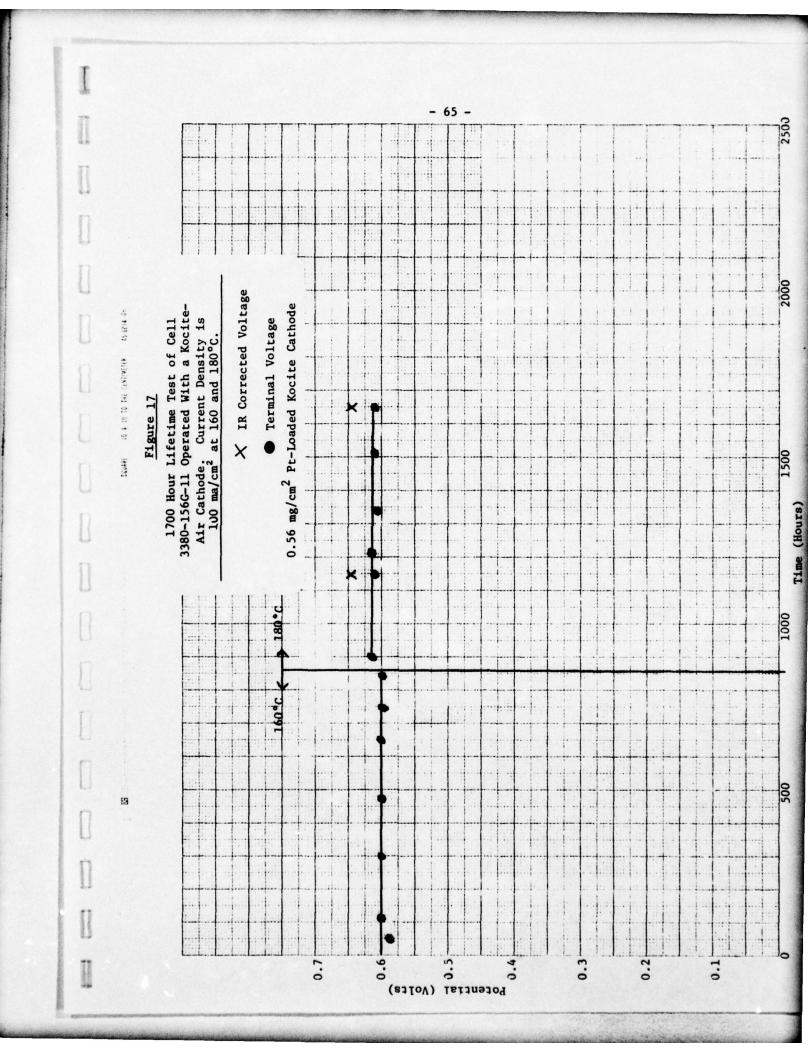
At UOP, cells containing cathodes fabricated from electrocatalyst batch 3380-156G have been running with excellent stability. An example of the performance of such a cell is shown in Figure 16. With the Kocite electrode used as an air cathode, a steadily increasing performance was obtained at 160°C for 1700 hours. After 1700 hours this cell had the best terminal voltage of any cell with a Kynol matrix at 160°C, 0.638 V at 100 ma/cm². (Polarization curves for this cell were shown in Figure 6.) The long term performance of another cell is shown in Figure 17. This cell has run for 800 hours at 160°C and then 1500 hours at 180°C with a terminal voltage over 0.61 V at 100 ma/cm² for the time at 180°C. All of the above cells were still in operation at the time of this report.

The cell with the highest terminal voltage, ERC's SiC-3 was stable at 180°C for 225 hours at 0.66 V with 100 ma/cm² current density as shown in Figure 10. At that time cross gas leakage occurred in the matrix









and the cell was shut down. No electrode instability was evident in the cell and improvements in the matrix should allow Kocite electrodes to operate stably at high performance levels for much longer times.

4.5 Results of the Structure Parameter Variation

4.5.1 Introduction

The main effort during this contract period has been to optimize both the electrocatalyst and the electrode structure. The emphasis has been on obtaining systematic performance data of electrodes fabricated from the two large electrocatalyst batches, 3380-125B and 3380-156G. Five parameters have been systematically varied during the course of the optimization program; platinum loading, teflon content, catalyst layer thickness, catalyst layer density, and cell operation temperature. The effect of varying these parameters on cell performance will be discussed in this section. Where possible, the optimum value or range of values will be identified for these parameters.

4.5.2 Platinum Loading

Platinum loadings of the electrodes used in this program have been in the range from 0.22 to 0.58 mg/cm² for electrodes made from both electrocatalyst batches 3380-125B and 3380-156G. Normally, electrodes had a nominal Pt loading of either 0.25 or 0.50 mg/cm². Within this range electrode performance is nearly proportional to Pt loading. At 100 ma/cm² current density and 160°C, the average

difference in the IR corrected voltage between cells with air cathodes having either a 0.25 or a 0.5 mg/cm² Pt loading was ~40 mV. The Tafel slope of these cells was 120 to 140 mV/decade. If the current is proportional to the platinum loading, then the voltage increase for doubling the platinum loading should be

130 mV/decade X log 2 ≃40 mV, (6) in agreement with the measured value.

The degree to which cell performance is proportional to Pt loading is shown in the polarization curves plotted in Figure 18. In this figure, cell voltage has been plotted as a function of the current per gram of platinum or the platinum-specific current. If the performance was proportional to the platinum loading, all the curves should be superimposed. For the best cells at each Pt loading, the relation holds very well. The platinum specific polarization points fall within a zone about 10 mV wide for cells having electrodes loaded between 0.22 and 0.56 mg/cm² Pt.

4.5.3 Teflon Content

To optimize the electrode structure, the teflon content of the electrodes has been varied in this study from ~15 to 50 wt.% of the unleached Kocite material. The results (4) indicate that electrodes with lower teflon loadings have higher performance levels and reach their maximum performance more quickly than electrodes having higher teflon loadings. For electrodes made from either the 3380-125B or the 3380-156G electro-

catalyst batches, the best performance was obtained with electrodes having a 20 or 30 wt.% teflon content. Attempts to operate at still lower teflon loadings failed because of flooding between the catalyst layer and the carbon paper support. This flooding caused the detachment of the catalyst layer from the support. This problem can probably be reduced by using a higher bonding pressure during electrode fabrication.

One possible reason that the electrodes with lower teflon loadings operate better than ones with higher loading is that with leaching, the weight percentage of teflon drastically increases. For an electrode containing electrocatalyst 3380-156G, a 50 wt.% teflon content becomes a 78 wt.% teflon content after leaching.

20 and 30 wt.% teflon loads become respectively 46 and 61 wt.% after leaching. (The teflon contents of electrodes after leaching are listed in Tables VIII and IX.) Thus the electrodes with the better performance have teflon contents which have a weight ratio of about 1:1 teflon to leached electrocatalyst. This is consistent with ERC's practice of using 50 wt.% teflon in their platinum-impregnated carbon-black electrodes. The optimum teflon content appears to be the loading which has about equal weights of teflon and electrocatalyst after the leaching process.

4.5.4 Electrocatalyst Loading

A Kocite electrocatalyst loading of 5 mg/cm² has been standard for most of the Kocite electrodes fabricated during the present contract period. Though this loading is relatively large in comparison with platinum black or platinum-doped carbon-black electrodes, there is no indication that a thinner catalyst layer with a higher platinum concentration produces any performance improvement. The proportionality of performance to platinum loading discussed in Section 4.5.2 indicates that the same percentage of platinum is being utilized in all electrodes for which performance data are plotted in Figure 18.

A comparison between electrodes with 5 mg/cm² of electrocatalyst 3380-125B and 2.5 mg/cm² of electrocatalyst 3380-156G is given in Table XV. Each electrode has about the same platinum loading, ~0.25 mg/cm². The average IR-free voltage at 100 ma/cm² of each group of electrodes is listed for both air and oxygen performance. The small differences between the average (<5 mV) indicates that the same percentage of the catalyst layer contributes to the performance of each cell.

4.5.5 Catalyst Layer Density

For the cells listed in Tables VIII and IX the electrodes were fabricated by bonding the catalyst layer to the carbon paper backing at "medium" density (100 psi pressure). ERC found this procedure suitable for machine-rolled platinum-doped carbon-black electrodes and it was used with little variation for the Kocite electrodes. Earlier in the program, some of the electrodes made from electrocatalyst 3380-125B were fabricated by a different

Table XV

Comparison of the Performance of Electrodes with Differing Catalyst Loadings

Average Air Cathode Voltages

Electrode ^b 3380-125B	Catalyst Loading (mg/cm ²) 4.4	Pt Loading (mg/cm ²) 0.22	Average Voltage (V) 0.594

Average O₂ Cathode Voltages a

<u>Electrode</u> ^b	Catalyst Loading (mg/cm ²)	Pt Loading (mg/cm ²)	Average Voltage (V)
3380-125B	4.4	0.22	0.690
3380-156G	2.6	0.26	0.685

^aIR Corrected voltages at 150°C and 160°C at 100 ma/cm² current density.

b3380-125B Cells - UOP 21, 24, 25, 26, 28 3380-156G Cells - UOP 1, 2, 4 and ERC 85, 87, 91

process that produced a less dense (low density) catalyst layer. These electrodes however tended to separate from the backing material during prewetting. A similar problem was encountered with the low teflon content (~15 wt.%), medium density electrodes and was discussed in Section 4.5.3. The adherence of the catalyst layer to the backing material was insufficient to prevent electrolyte from getting between them. The electrolyte floods the back of the electrode rather than the catalyst layer itself. Use of higher bonding pressures should eliminate the problem.

4.5.6 Cell Operating Temperature

Cell operation at higher temperatures has the advantage of improved cell performance and substantially greater tolerance of the anode to poisoning from CO in the fuel. In cells with Kocite air cathodes, the average improvement in performance approaches 1 mV/°C at 100 ma/cm² current density. The increase results from faster diffusion and a higher oxygen reaction rate. For pure oxygen the gain is somewhat less because there is a minimal diffusion penalty to overcome. While no problems are seen in operating cells at 150 to 160°C, ERC makes no representation as to the stability of its cell components, particularly the Kynol matrix, at 180°C or above. With careful control of the water balance and electrolyte replacement, cells do appear to operate quite stably at 180°C as shown by Figure 15 in which the cell ran for 2500 hours as an air cathode. With the proper silicon carbide matrix, these

cells should operate stably at temperatures of 180°C or higher. Although platinum sintering should be more of a problem at the higher temperatures, there has been no indication from the 180°C lifetime tests completed to date that sintering is limiting cell performance.

4.6 Summary of Results

Over this contract period, several important results have been obtained which are listed below.

(A) Electrode Performance

The performance levels of cells using Kocite electrodes as cathodes have been dramatically improved during this contract period. The best cell used an experimental SiC matrix and operated stably on air with terminal and IR corrected voltages of 0.66 and 0.70 V, respectively, at $100~\text{ma/cm}^2$ and $180\,^\circ\text{C}$. The Pt-loading of this cathode was $0.54~\text{mg/cm}^2$. At this current density 0_2 gains have been reduced to 70 to 80 mV routinely and in some cases to 60 mV. The performance levels obtained with Kocite electrodes are comparable to the levels obtained by ERC using their Pt-impregnated carbon-black electrodes.

(1) According to ERC experience, the use of a silicon carbide rather than Kynol matrix improves cell performance ∿40 mV at 100 ma/cm² and 150°C. The best cell to date with a Kynol matrix used a 0.42 mg/cm² Pt-loaded Kocite cathode and had a terminal voltage of 0.646 V on air at 100 ma/cm² and 180°C. This indicates that still higher air cathode performance may be expected from Kocite electrodes in cells with a SiC matrix.

- (2) Cells with cathodes from the same electrode batch have given highly reproducible results.
- (3) Cells have run stably as air cathodes at 100 ma/cm² for periods up to 2500 hours at 180°C and 4000 hours at 150°C. At the time of this report, these cells were still operating.
- (4) A cell with a Kocite anode has run stably for over 500 hours at 180°C with a current density of 100 ma/cm². A cell with Kocite electrodes as both the anode and cathode has operated stably for over 1200 hours.
- (5) Kocite anodes have shown greater short term resistance to CO poisoning than 2 mg/cm² platinum black anodes when used with 5% CO in H₂ fuel gas. At 180°C, the platinum black electrode had 2 to 5 times the voltage loss of the Kocite-electrode. This difference was more pronounced at lower temperatures.

(B) Electrode Structure Optimization

The program to optimize the structure of the Kocite electrodes has yielded significant improvements in both the stability and performance levels of these electrodes. The results of this program indicate the following:

- (1) The best performance results were obtained with electrodes having a teflon content of 20 to 30 wt.% of the fabricated electrode or ∿1:1 weight ratio with the leached Kocite-derived electrocatalyst.
- (2) Electrodes with medium density (100 psi bonding pressure) catalyst layers have better performance characteristics than electrodes with low density layers. For electrodes with the lowest

teflon contents, higher pressure must be used during electrode fabrication to bond the catalyst layer to the carbon paper backing.

- (3) The Al₂O₃ substrate is leached from the electrocatalyst leaving a carbonaceous pyropolymer material with a surface area as high as 750 m²/g. The leaching does not appear to impair the lifetime performance of electrodes containing the leached electrocatalyst.
- (4) The cell performance levels are proportional to the platinum loading in the range 0.2 to 0.6 mg/cm² platinum. Thicker layers of a less heavily platinum loaded catalyst may give comparable results.

(C) Platinum Crystallite Sintering

The amount of Pt crystalline growth at 180°C has been determined by X-ray diffraction techniques for both electrocatalyst powders soaked in H₃PO₄ and Kocite electrodes operated in fuel cells.

- (1) For catalyst powders with no applied potential the sintering rate appears to depend on the platinum to carbon ratio of the catalyst with higher Pt-loaded powders sintering more rapidly. For the same value of Pt/C, the rate of sintering was less for Kocite electrocatalyst powders than for ERC Pt-doped carbon black powders.
- (2) For catalysts in electrodes operated as air cathodes in fuel cells, the sintering was not significant at 160°C or below. At 180°C the results were similar to the results for the powders with the catalysts having a higher value of Pt/C showing greater sintering. Pt sintering did not appear to limit electrode performance, since the lifetime tests did not show performance loses matching the rate of platinum sintering.

V. CONCLUSIONS

Based on the improved results obtained during the latter part of the contract period, several conclusions concerning low cost fuel cell electrodes using Kocite-derived materials can be stated.

- (A) Kocite electrodes can be used as stable cathodes and anodes at 180°C. Cells with both a Kocite anode and cathode operate comparably with those containing a Pt black anode.
- (B) Electrode optimization has progressed to the point where terminal voltages of 0.66 V at 100 ma/cm² and 180°C have been achieved with a cell having 0.5 mg/cm² Pt-loaded Kocite air cathode. Electrode performance is proportional to the platinum loading and varies with temperature at the rate of ∿1 mV/°C from 140 to 180°C. The teflon content of the catalyst layer should be in the ratio of ∿1:1 with the carbonaceous pyropolymer component of the electrocatalyst.
- (C) A number of cells containing cathodes from the best electrode batch were run under the same conditions. The similarity of cell performance indicated that Kocite electrodes can perform reproducibly.
- (D) The rate of sintering of platinum particles on Kocite-derived electrocatalysts was determined by X-ray diffraction techniques. Sintering rates for the Kocite-derived electrocatalysts were found to be lower than on carbon-black electrocatalysts of the same platinum loading.

VI. RECOMMENDATIONS

To further improve the performance of Kocite-containing electrodes and continue their development for use in H₃PO₄ electrolyte fuel cells, the following recommendations are made:

- (A) Prepare and test electrocatalysts in which the Al₂O₃ has been leached either before or after impregnation. Electrocatalysts with high Pt dispersion should then be fabricated into electrodes and tested in model fuel cells.
- (B) Determine if the electrode structure should be modified to obtain maximum performance from the leached electrocatalysts.
- (C) Test Kocite electrodes as anodes and cathodes at 180°C for extended periods (5000 hr. or more). Continue the Pt sintering experiments to relate the sintering rate to the electrocatalyst composition and preparation method.
 - (D) Produce and test electrodes of the size used in fuel cell stacks.
 - (E) Fabricate and test a full size fuel cell stack.

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Hyattsville, MD 20782

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Office of Naval Research
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Naval Ship Systems Command
Department of the Navy
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Washington, DC 20360

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Murray Hill, NJ 07974

Mr. George Ciprios (1)
Exxon Research & Engineering
PO Box 8
Linden, NJ 07036

General Electric Company (1) 50 Fordham Road ATTN: L. J. Nuttall Applications Engineer Bldg. 1A Wilmington, MA 01887

L. G. Marianowski, Manager (1) Energy Conversion & Storage Research Institute of Gas Technology 3424 S. State Street Chicago, II. 60616

P. L. Howard Associates, Inc. (1) Millington, MD 21561 Arthur D. Tevebaugh, Director (1) Coal Technology Programs Argonne National Laboratory Bldg. 205 9700 South Cass Avenue Argonne, IL 60439

Massachusetts Institute of Technology (1) ATTN: Professor H. P. Meissner Cambridge, MA 02138

Pratt & Whitney Aircraft Division (1) United Aircraft Corporation ATTN: Mr. W. H. Podolny 400 E. Main Street East Hartford, CN 06108

The Standard Oil Company (1) Research Center 4440 Warrensville Center Road ATTN: Dr. Robert A. Rightmire Cleveland, OH 44128

Science Applications, Inc. (1) ATTN: Dr. Herbert P. Silverman 1200 Prospect Street PO Box 2351 La Jolla, CA 92038

Dr. Douglas N. Bennion (1)
Energy & Kinetics Department
School of Engineering & Applied Science
5532 Boelter Hall
University of California
Los Angeles, CA 90024

Union Carbide Corporation (1)
Parma Research Center
PO Box 6166
ATTN: Dr. R. Brodd
Parma, OH 44101

University of Florida (1)
Department of Chemical Engineering
PO Box 3027
ATTN: Professor R. D. Walker
Gainesville, Florida 32601

Energy Research Corporation (1) ATTN: Dr. B. S. Baker 3 Great Pasture Road Danbury, CN 06810

Mr. Norman Rosenberg (1)
US Department of Transportation
Transportation Systems Center
55 Broadway
Cambridge, MA 02142

Dr. R. T. Foley (1) Chemistry Department The American University Washington, DC 20016

Dr. S. B. Brummer (1) Director of Physical Research EIC, Inc. 55 Chapel Street Newton, MA 02158

Director, Technical Information (1) Advanced Research Projects Agency 1400 Wilson Blvd. Arlington, VA 22209

Dr. D. C. Olson (1) Shell Development PO Box 1380 Houston, TX 77001

Dr. R. A. Wynveen President Life Systems, Inc. 24755 Highpoint Road Cleveland, OH 44122

Electric Power Research Institute ATTN: A. P. Fickett PO Box 10412 Palo Alto, CA 94304

State University of New York at Buffalo ATTN: Professor Stanley Bruckenstein Chemistry Department Acheson Hall, SUNY/AB Buffalo, NY 14214

Hugh J. Barger, Jr. Box 2232 Davidson, NC 28036 Dr. Ralph Roberts
Energy Resources & Environmental Systems
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The MITRE Corporation Mail Stop W-389
Westgate Research Park
McLean, VA 22101

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